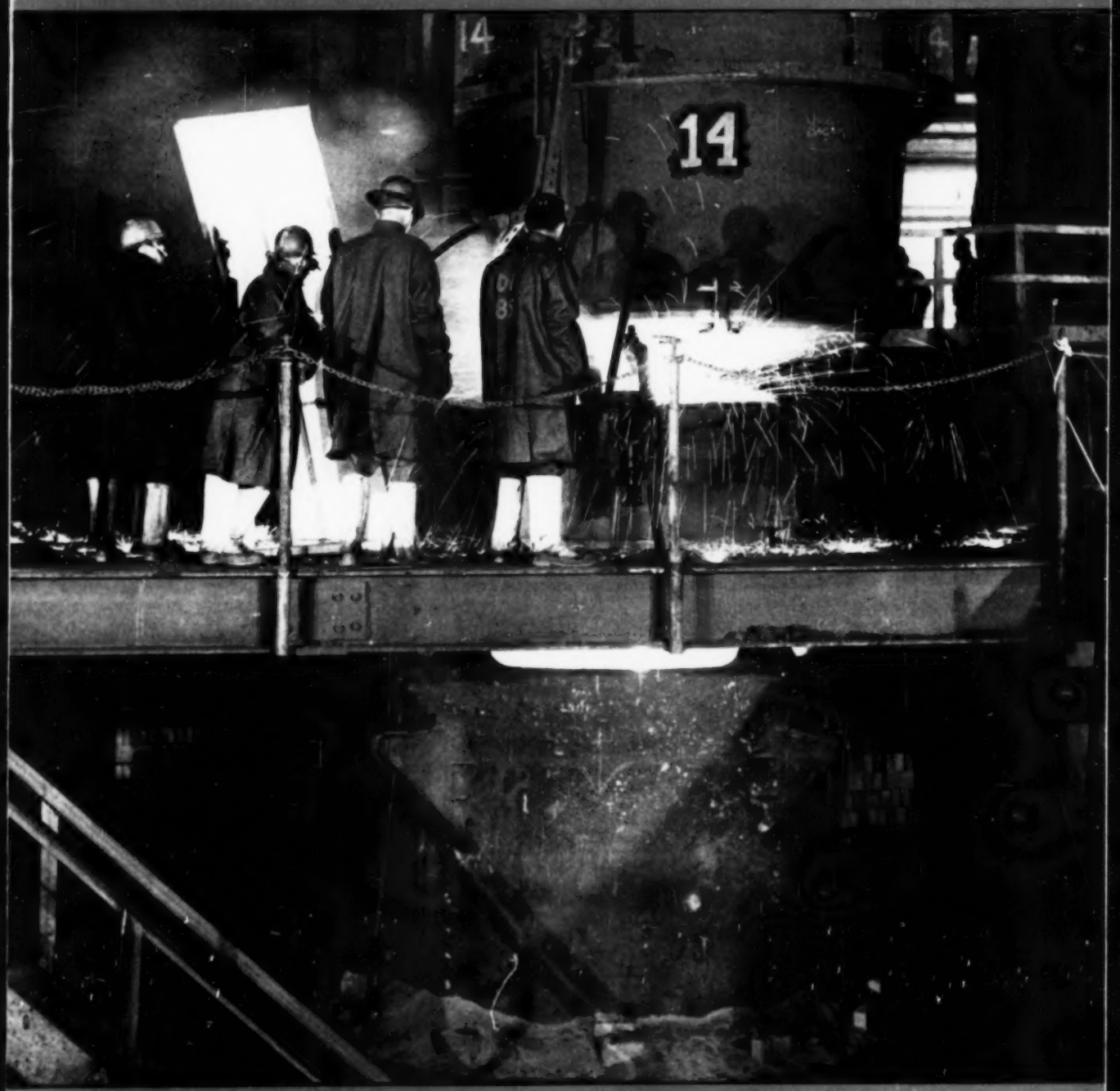
FEBRUARY, 1953
IN TWO SECTIONS—SECTION I

Journal of METALS

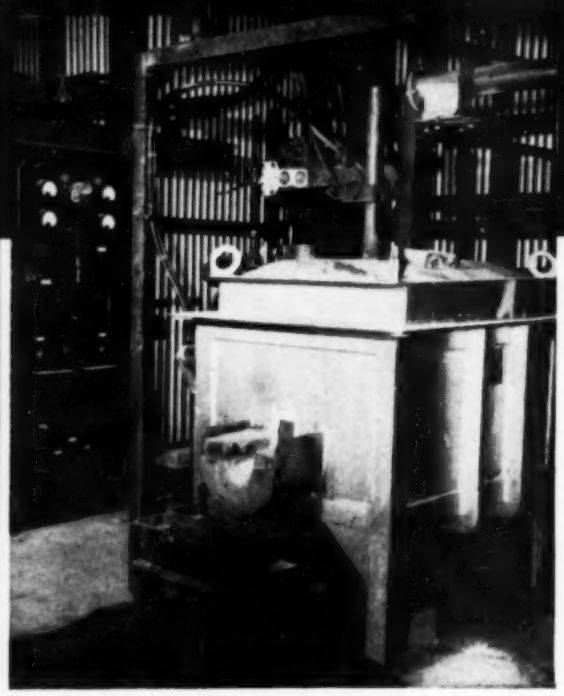


February JOURNAL OF METALS Highlights:

"Titanium Symposium" - p. 130
"Research In Progress" - p. 153
"Arc Furnace Equipment at Kennecott" - p. 197

Weirton Steel recovers scarce tin and steel scrap with the help of three *Lectromelt* * furnaces

Two Lectromelt Reduction Furnaces handle final recovery of tin from scrap at Weirton Steel Co., Division of National Steel Corporation, Weirton, West Virginia.



Sludge formed in tin mill operations emerges from this third Lectromelt Furnace as commercially pure tin.

Baled scrap from the tin mill and other sources is sawed open to expose a maximum surface to the detinning bath—a 50% solution of sodium hydroxide containing sodium nitrate. The tin dissolves and precipitates as a slurry, which is filtered out and treated to form tin oxide. The bare steel is ready for remelting.

A mixture of this oxide and fine anthracite coal is charged into one of two Lectromelt Furnaces, where carbon unites with the oxygen to free the tin. Furnaces are tapped on a 6-hour cycle and tin is cast in 100-pound pigs for shipment to the tin mill.

A second recovery plant at the tin mill recovers the tin from the sludge that accumulates in the plating cells of the electrolytic lines. Thus scarce tin is salvaged in both operations and steel scrap, which otherwise would be undesirable because of its tin content, is reclaimed.

For information on Lectromelt Furnaces, write Pittsburgh Lectromelt Furnace Corporation, 326 32nd Street, Pittsburgh 30, Pa.

Manufactured in . . . CANADA: Lectromelt Furnaces of Canada, Ltd., Toronto 2 . . . ENGLAND: Birlec, Ltd., Birmingham . . . FRANCE: Stein et Roubaix, Paris . . . BELGIUM: S. A. Belge Stein et Roubaix, Bressaux-Liege . . . SPAIN: General Electrica Espanola, Bilbao . . . ITALY: Forni Stein, Genoa.

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WHEN YOU MELT... *Lectromelt*

Journal of METALS

VOL. 5, NO. 2 FEBRUARY, 1953

IN TWO SECTIONS — SECTION 1

COVER

Bethlehem Steel Co. used heats from two open hearth furnaces, poured in sequence, to form the 275-ton ingot that will eventually be part of a column for the 50,000-ton forging press being constructed by Loewy Construction Co. for Wyman Gordon. See page 129.

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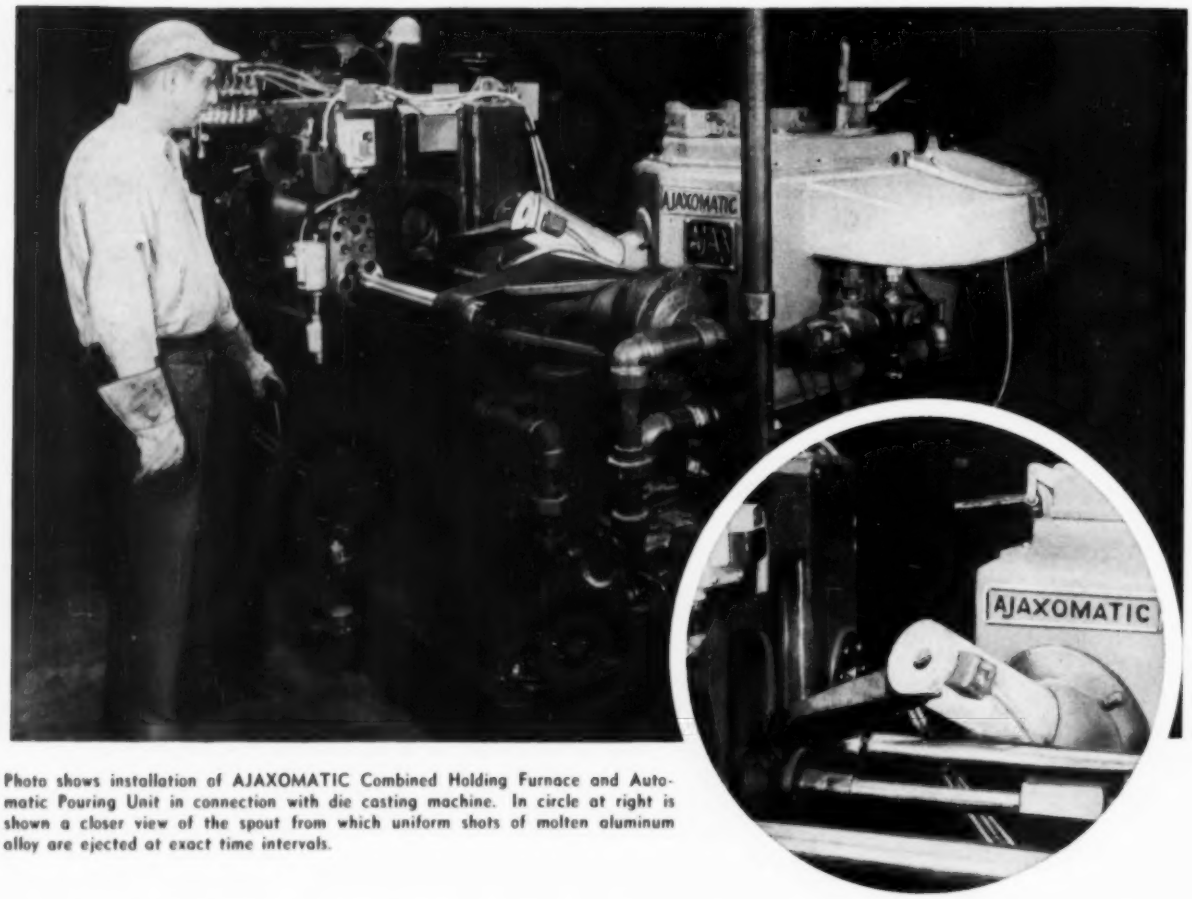

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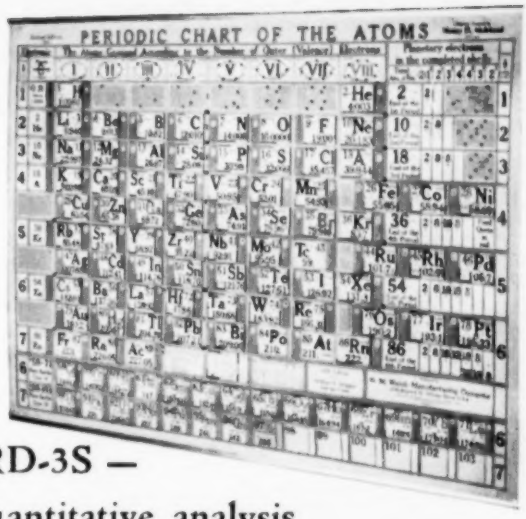

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MEET THE AUTHORS

Edgar Marburg (p. 157) is with the research and development laboratory of the U. S. Steel Corp., Pittsburgh. A native of Philadelphia, Mr. Marburg graduated from the University of Pennsylvania (B.S.) and Massachusetts Institute of Technology (M.S.). For six years he was in the Corps of Engineers, U. S. Army. He resigned in 1920 and joined the Aluminum Co. of America at the Boston sales office. For two years Mr. Marburg was associated with the Jones & Laughlin Steel Corp., Aliquippa, Pa. From 1929 to 1938 he was chief metallurgist for the Carnegie Illinois Steel Corp. Mr. Marburg is active in the YMCA and his varied hobbies include carpentry, landscape gardening and stone-wall building, fishing, and poker (occasionally).

EDGAR MARBURG

H. G. G. WHITTON

H. G. G. Whitton (p. 197) is a graduate of University of Toronto (1925, B.A.Sc.). Born in Manitoba, he is presently residing at Magna, Utah. Following graduation, Mr. Whitton joined the mine engineering staff of the International Nickel Co. of Canada. In 1933 he was transferred to the copper refining div., Copper Cliff, Ont. He was promoted to assistant superintendent of the casting dept. in 1934 and then became departmental superintendent in 1938. In 1948 he resigned for private practice. At this time he assisted in starting new electric-arc, copper melting units at the Reading Tube Corp., American Smelting & Refining Co., and the Canadian Copper Refiners. In 1949 Mr. Whitton joined the operating staff of the Kennecott Copper Corp., Utah refinery, where he is in charge of the new casting dept.

H. A. Shaw (p. 197), AIME Member of the Utah Section, was born in Seattle. After his graduation from the University of Washington he did post-graduate work at Massachusetts Institute of Technology. He started his professional career in the laboratory of the Tacoma smelter of the American Smelting & Refining Co. In 1932 he was transferred to the operating dept. to become an assistant superintendent of the plant. Mr. Shaw went to Chile in 1940 as assistant smelter superintendent for the Braden Copper Co., a subsidiary of Kennecott Copper Corp. He was promoted to smelter superintendent in 1944 and held that position until December 1947, when he was transferred to New York City. Two years later Mr. Shaw went to Salt Lake City and is presently refinery superintendent for the Utah Copper Div., Kennecott Copper Corp. Rearing four sons takes up quite a bit of his spare time, but he manages to play golf frequently.

H. A. SHAW

M. A. HUNTER

M. A. Hunter (p. 130) is Dean Emeritus of Rensselaer Polytechnic Institute, Troy, N. Y. Dr. Hunter attended the University of New Zealand (B.Sc., M.A.) and University of London (D.Sc.). He has also done post-graduate work at Gottingen University, the Sorbonne, and Technische Hochschule, Karlsruhe. In 1949 he received the degree Honorary Doctor of Engineering from Rensselaer. He started his professional career in the research laboratories of the General Electric Co., Schenectady. In 1908 he joined the staff of Rensselaer as professor of electrochemistry. In 1933 he was named head of the dept. of electrical engineering and physics. Dr. Hunter was head of the dept. of metallurgical engineering from 1935 to 1947. He became dean of the faculty in 1943. He was also director of research and consulting engineer for the Driver-Harris Co. and L. E. Gurley Co. Dr. Hunter is a member of the American Chemical Society, AIME, American Electrochemical Society, ASM, and AAAS. He has also contributed to many scientific publications and presented numerous papers before AIME.

John N. Dick (p. 133), colonel in the U. S. Air Force, was born in New York in 1903. His present assignment is chief, materials and components div., directorate of industrial resources, Office of the Deputy Chief of Staff, Materiel, Washington, D. C. During his army career Col. Dick has served in the Office of the Chief, Chemical Corps as assistant executive officer. He assisted in the early development of the Chemical Procurement Program during the emergency period. He also gained procurement experience in civilian activities including positions as industrial relations director, personnel and public relations director, production manager, director of foreign trade zones project. Col. Dick was also a personal representative of the late Mayor F. H. LaGuardia of New York, assigned to Washington to negotiate the grant with the Foreign Trade Zones Board. He has organized, aided and established several divisions connected with civil defense. Col. Dick is a graduate of the Armed Forces Industrial College. In his free time he enjoys golf, swimming, and landscape painting.

Bruce M. Shields (p. 180) has been associated with the U. S. Steel Co. since 1942 when he joined the Homestead Works as a metallurgical observer. He has been development metallurgist, research metallurgist, successively. At present he is chief development metallurgist at the Duquesne Works. Mr. Shields is a graduate of Carnegie Institute of Technology (B.S.) and Massachusetts Institute of Technology (M.S.). He is a member of the Pittsburgh Section, AIME, and has presented discussions at Open Hearth and Electric Furnace meetings.

B. M. SHIELDS

B. S. MESICK

Benjamin S. Mesick (p. 136) is now commanding officer of the Watertown Arsenal, Mass. Prior to this appointment he had been chief of research and materials branch, ordnance research and development div., Washington, D. C. Prior to entering West Point in 1920, Col. Mesick had attended Cornell University. Following his graduation from West Point, he served in the Coast Artillery Corps for five years. Since 1929 he has been with the Ordnance Corps, serving at various installations in this country and abroad during World War II. He also earned a Master of Science degree in mechanical engineering from Massachusetts Institute of Technology and a degree of Doctor of Science from MIT. In 1945 Col. Mesick was officer-in-charge of the ordnance research and development suboffice (rocket) at the California Institute of Technology. He remained here until 1949 when he became commanding officer of the Sierra ordnance depot, Calif.

T. E. Perry (p. 150) was born in Evanston, Ill. and graduated from the University of Illinois in 1948 (B.S.). He joined the Republic Steel Corp. in 1948 as stainless metallurgist. He later became development engineer in titanium and is now contact metallurgist for titanium. As his hobbies he counts hunting, fishing, and golf.

T. E. PERRY

E. L. BEARDMAN

Edward L. Beardman (p. 138) has been a civilian engineer in the Office of Naval Material since 1946. He is presently materials engineer and head of the metals and minerals section, production div., Office of Naval Material. Born in Sharon, Pa., Mr. Beardman is a graduate of Carnegie Institute of Technology. He has done graduate work at Carnegie and Case Institute of Technology. After graduation he was associated with the metallurgical dept. of Youngstown Sheet & Tube Co. In 1934 he joined the American Steel & Wire Co., Cleveland, as a laboratory assistant. During his employ with this company he successively held the positions of plant metallurgist, foreman of the stainless steel dept., and assistant director of the metallurgical laboratory. Mr. Beardman was granted a leave of absence in 1941 to accept a position in the Navy Dept. as metallurgical engineer. He was commissioned a lieutenant in 1942 and returned to inactive duty in 1946 with the rank of commander.

Lee S. Busch (p. 146) is now senior metallurgist, head of central metallurgical engineering, for P. R. Mallory, Indianapolis. Born in Indianapolis, Mr. Busch is a graduate of Purdue (B.S., Ch.E.). After graduation he was associated with National Malleable & Steel Castings as process metallurgist. In 1943 he joined P. R. Mallory. Mr. Busch is a member of AIME and ASM, and has been a Chairman of the AIME Powder Metallurgy Committee. Hunting, fishing, and photography occupy him in his spare time.

C. S. Roberts (p. 203), a native of Rupert, Vt., graduated from Rensselaer Polytechnic Institute and also did graduate work at Massachusetts Institute of Technology. As his hobbies, Mr. Roberts counts photography and music. He is presently connected with the Dow Chemical Co., Midland, Mich. in the physical metallurgy section.

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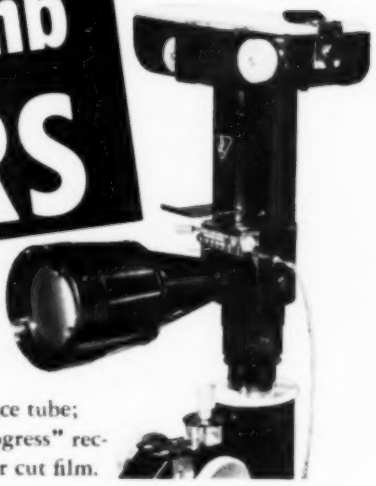

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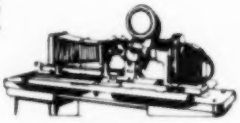

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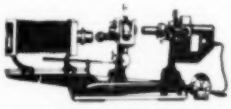

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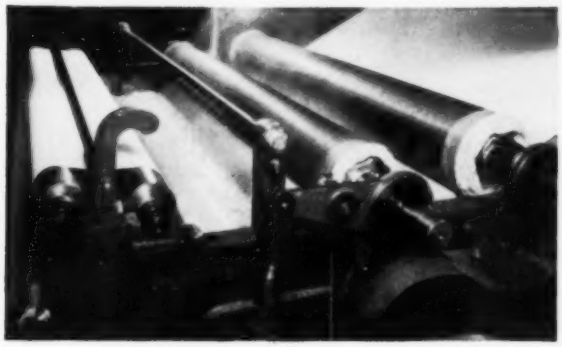

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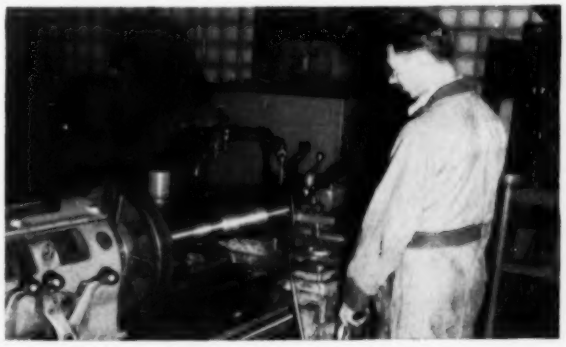

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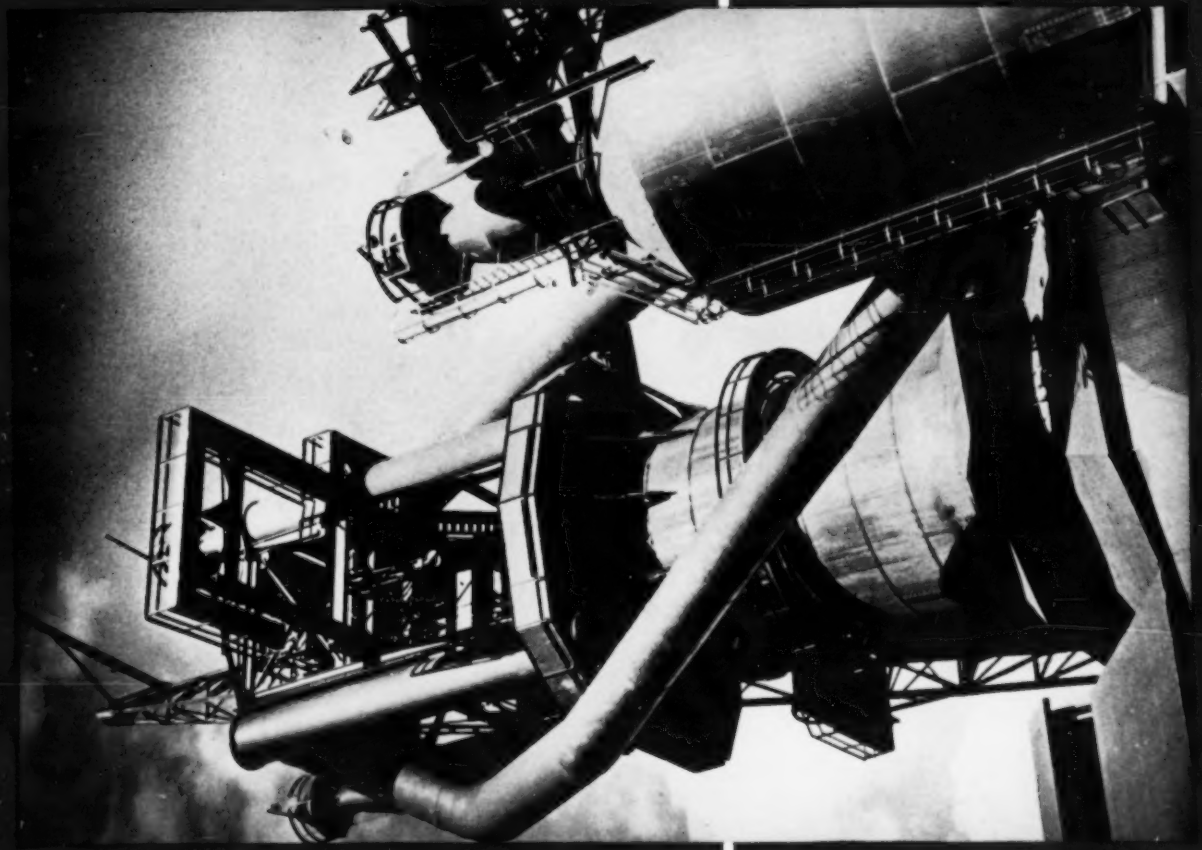

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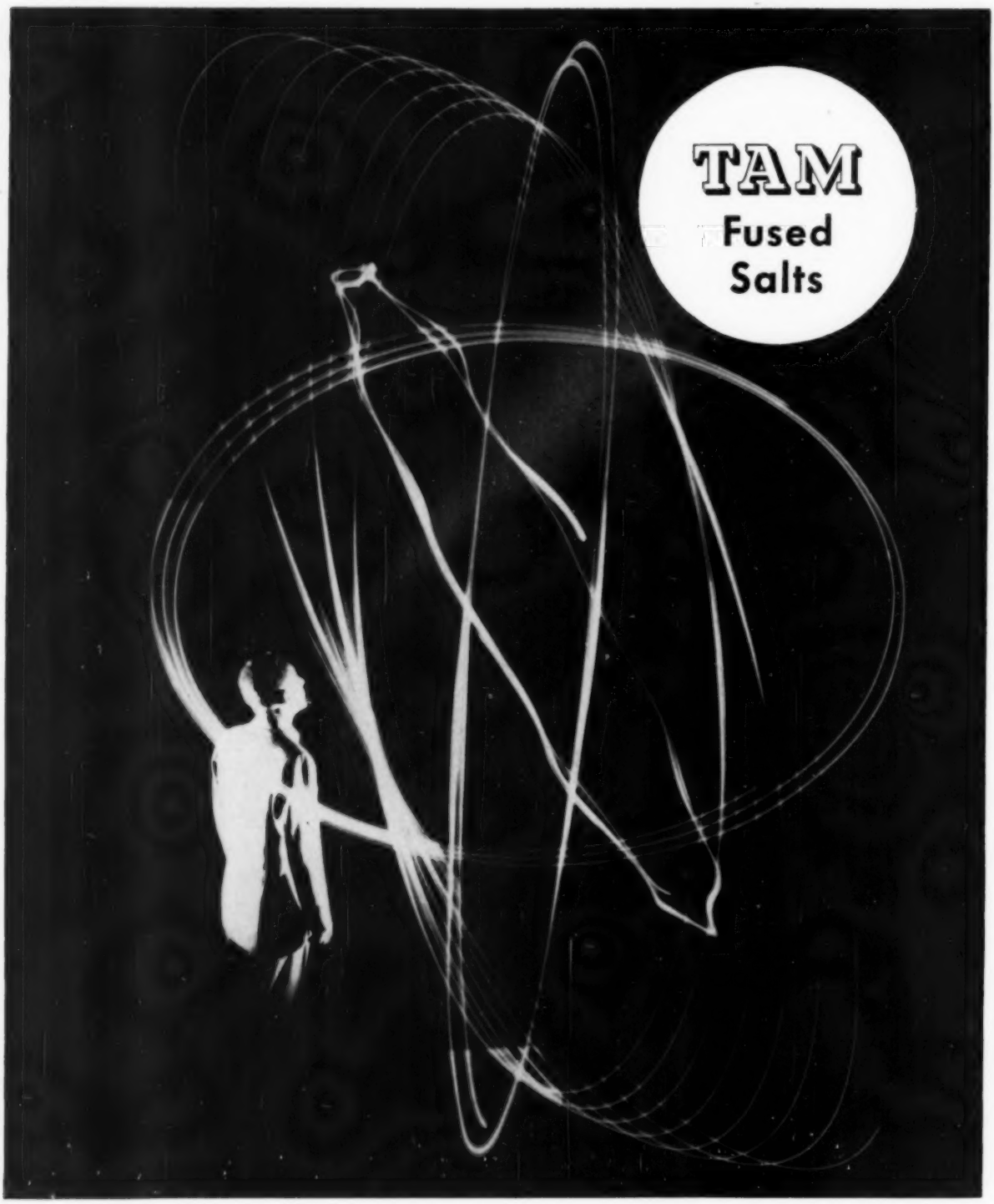

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1—BUFFING COMPOSITION: Greaseless composition adhering to the wheel face to form a heavy, fast drying head that does not fly off and remains firm even in the warmest weather is offered by *Hanson-Van Winkle-Munning Corp.* The composition also features a consistently-sized abrasive. Particles of exactly the same size act upon all parts of the work to produce a uniform finish.

2—CARBOTROL: This proportioning instrument enables the heat treater to set his atmosphere or furnace in equilibrium with any steel. Manufactured by *Lindberg Engineering Co.*, it permits the automatic control of the carbon potential of furnace atmospheres.

3—TEMPIL° PELLETS: These pellets are temperature sensitive tablets of calibrated melting points. There are 70 different pellets, covering the range from 113° to 2500°F, each indicating a specified temperature within a tolerance of ±1 pct of its rating. They find their widest use in furnace applications where their greater mass offers a more enduring signal for prolonged heating than a Tempilaq° or Tempilstik° mark. *Tempil° Corp.*

4—PENETRANT INSPECTION: New *Burton Mfg. Co.* magnifier black light complies with AFS MIL-I-6866 covering black lights used for fluorescent penetrant inspection

on metals, ceramics, castings, etc. Twin tubes produce prolific but harmless 3660A ultra-violet energy when directed upon the inspected surface. There is no back glare or heat. White fluorescent tubes may be used in the unit for high detail inspections.

5—TALK-A-PHONE: A new 20-w Redi-Power model has been announced by the *Talk-A-Phone Co.* Twelve, 20, 30, or 40 station capacity can be housed in the same cabinet with only 12 pushbuttons. It is self-compensating to deliver required power to all or a select group of

stations, supplying ample power to each station when called simultaneously as well as individually.

6—COIL BENDING: This semi-automatic machine for serpentine coil bending is announced by *Pines Engineering Co., Inc.* One movement of the operating lever initiates entire clamping and bending cycle. It performs a variety of short run work due to simplicity and quick and easy changeovers in setup.

7—HEAT TREATING: A 400 lb per hr automatic heat treating unit featuring 100 pct forced convection heating has been announced by *Ipsen Industries, Inc.* The unit operates at temperatures up to 1850°F and has complete automatic straight-through operation from heat through cooling or oil quench.

8—DIPBLACK: Improvements in process will produce a uniform, rich black finish on any assembled unit consisting of different types of iron and steel (mild carbon and spring steel). Dipblack does not affect dimensions or surface texture and will not chip, peel or scale during or after welding, soldering, bending, punching, stamping, or rolling. *Special Chemicals Corp.*

9—HEATED SCREEN CLOTH: A new method of heating screen cloth by electricity to prevent clogging or blinding when wet materials are screened was announced by *Hewitt-Robins Inc.* Voltages range between 5 and 15 v and amp from 1000 to 4000.

10—MOTOR: An outdoor weather protected motor carrying protection much further than splashproof design is available from *Allis-Chalmers Mfg. Co.* for semioutdoor and outdoor stations. Designed to keep wind-driven heavy moisture out of the windings, the intake air velocity has been reduced to less than 600 fpm.

11—BOOM: A 600-lb capacity *Yale & Towne* electric crane equipped with articulated platform is used for faster and easier maintenance of lighting and other overhead equipment both indoors and outdoors.

12—COIL STORAGE RACK: Storage space is conserved and equipment made more flexible in a new stacking type coil rack. It has an easily removable tray or shelf that makes it possible to place two rows of small diameter coils, one above the other, in a conventional rack. The frame can be lifted out of the rack making the rack suitable for use in handling larger diameter coils. *Equipment Mfg., Inc.*

13—HARDNESS TESTER: This tester permits metal producing and metalworking plants to obtain superficial readings with a portable instrument. It gives direct dial

reading in Rc 15N scale, 70-95. They are available in Rc A, B. C. 15N scales and Br low and medium scales. *Newage International, Inc.*

14—PLATFORM TRUCK: New Transveyor riding-type electric platform truck permits 6-ft aisle operation. Compact, lightweight, maneuverable materials handling unit, with 4000-lb capacity, in 6, 7, 9, or 11 in. platform heights; platform lengths vary from 36 to 72 in. Provides load equalization regardless of floor conditions. *Automatic Transportation Co.*

15—WELDING EQUIPMENT: Welding equipment of German design is now available from the *American Messer Corp.* The full line of Messer equipment incorporating a complete line of gas and electric welding equipment, automatic cutting machines, oxygen plants and acetylene generators is being handled.

Free Literature

20—SPRAYWELD: Bulletin describing spraywelder and sprayweld process is available from the *Wall-Colmonoy Corp.* Water turbine pump sleeves, acid sludge pump components and petroleum industry thermowells, that have been spray-welded to resist wear and corrosion are illustrated.

21—CONTOUR SHEAR: The *Wales-Strippit Corp.* tru-edge contour shear is illustrated in catalog TS. Inside cutting, beading and flanging of sheet metal parts up to 10 gage mild steel and 11 gage stainless steel are featured.

22—METAL SHOT: The increasing use of metal shot as weighting or back-up material, particularly in shell molding, is described in bulletin issued by *Metals Disintegrating Co.*, Harrison Abrasive Div.

23—CYACOR RESINS: These resins, their use as core binders, are listed in booklet released by *American Cyanamid Co.*, Plastics Dept. Formulations, mixing procedure, baking procedure, and storage are discussed.

24—CRUCIBLES: The latest information of recent developments in Amera-Mag steel fabricated crucibles for magnesium melting is contained in a brochure available from *American Tank & Fabricating Co.*

25—MEEHANITE: Case histories showing how critical material shortages have been solved by use of Meehanite castings are given in booklet published by *Meehanite Metal Corp.* Also included are alphabetical tabulations showing specific replacements of alloyed irons and steels, brass, bronze, forgings, etc.

26—WELDMENTS: Fabricated steel weldments, composite welded assemblies of fabricated steel plate and castings, and cast-welds assembled entirely of castings are the subject of a 6-page bulletin issued by *Continental Foundry & Machine Co.* Design principles, economy factors, and physical advantages are also given.

27—AL MELTING FURNACE: The complete line of Lindberg-Fisher gas and oil fired aluminum melting furnaces is described in new bulletin. Photographs of the various types of aluminum melting furnaces are shown; uses and specifications are listed. *Lindberg Engineering Co.*

28—ELECTRODE RAPPING: A new system of continuous, intensity controlled rapping for Cottrell electrostatic precipitators is described in bulletin. Explanation of how the M.I. rapper operates and a summary of features are included. *Research Corporation.*

29—BTU METER: Instrumentation data sheet No. 10.19-1 describes the operation and application of the Brown Btu meter, which simultaneously records differential temperature and flow of a liquid, and provides direct reading of Btu. *Minneapolis-Honeywell Regulator Co.*

30—AL SHEET MILL: A 24-page booklet has been published by *Reynolds Metals Co.* entitled *Welcome to the McCook Plant.* Equipment and operations at the firm's aluminum sheet mill are described.

31—DAMPERS: Louver, round, mixing, outlet, and fire dampers for regulation of air flow in industrial applications, electric, pneumatic, and manual damper operators are described in catalog 8502. *Minneapolis-Honeywell Regulator Co.*

32—TESTING MACHINES: Detailed information on accessories, instrumentation and tools for Universal testing machine is given in catalog 46 published by *Tinius Olsen Testing Machine Co.* Electronic recorders, electronic strain instrumentation, and mechanical extensometers are only a few of the topics covered.

33—CU-BASE ALLOY ROD: Handbook has been published by the *Copper & Brass Research Assn.* Pertinent data about free cutting brass and other copper base alloys in the form of rod for screw machine products are included.

34—AJAXOMATIC: Characteristics of this new combination induction holding furnace and pumping unit for use in die casting of aluminum and zinc alloys are described in folder. Photographs showing unit in operation, control cabinet, and installation diagram are included. *Ajax Engineering Corp.*

35—AB METAL ANALYST: A comprehensive 200 page catalog of metallurgical apparatus. Contains latest listing of cutters, grinders, mounting presses, polishers, metallographs, microscopes, cameras, testing machines, analytical apparatus, spectrographs, furnaces, accessories, and supplies, and 250 recommended books for the metallurgical library. *Buehler Ltd.*

36—HYDRAULIC PRESS: *R. D. Wood Co.* has re-issued a photographic book covering the company's facilities, methods, and equipment as related to hydraulic press and valve manufacture. The book is issued coincident with the firm's 150th anniversary.

37—PRECISION METAL PARTS: Catalog listing the small precision metal parts made by the Specialties Div. of the *Torrington Co.* is now available. Many parts are described and illustrated.

38—ELECTROPOLISHER: A bulletin is offered providing information on the theory and practice of electrolytic polishing of metallurgical samples together with description of the Buehler electro polisher. *Buehler Ltd.*

39—LIGHTING: *General Electric Co.* has issued the latest of its *See Better-Work Better* bulletins. Balanced brightness and sufficient lighting are the main theme of the new leaflet.

40—RETORT FURNACES: Accurate carbon control is possible with a *Hevi-Duty Electric Co.* vertical retort furnace. Bulletin HD-646 contains information on retort furnaces for carburizing, nitriding, dry cyaniding, and bright annealing.

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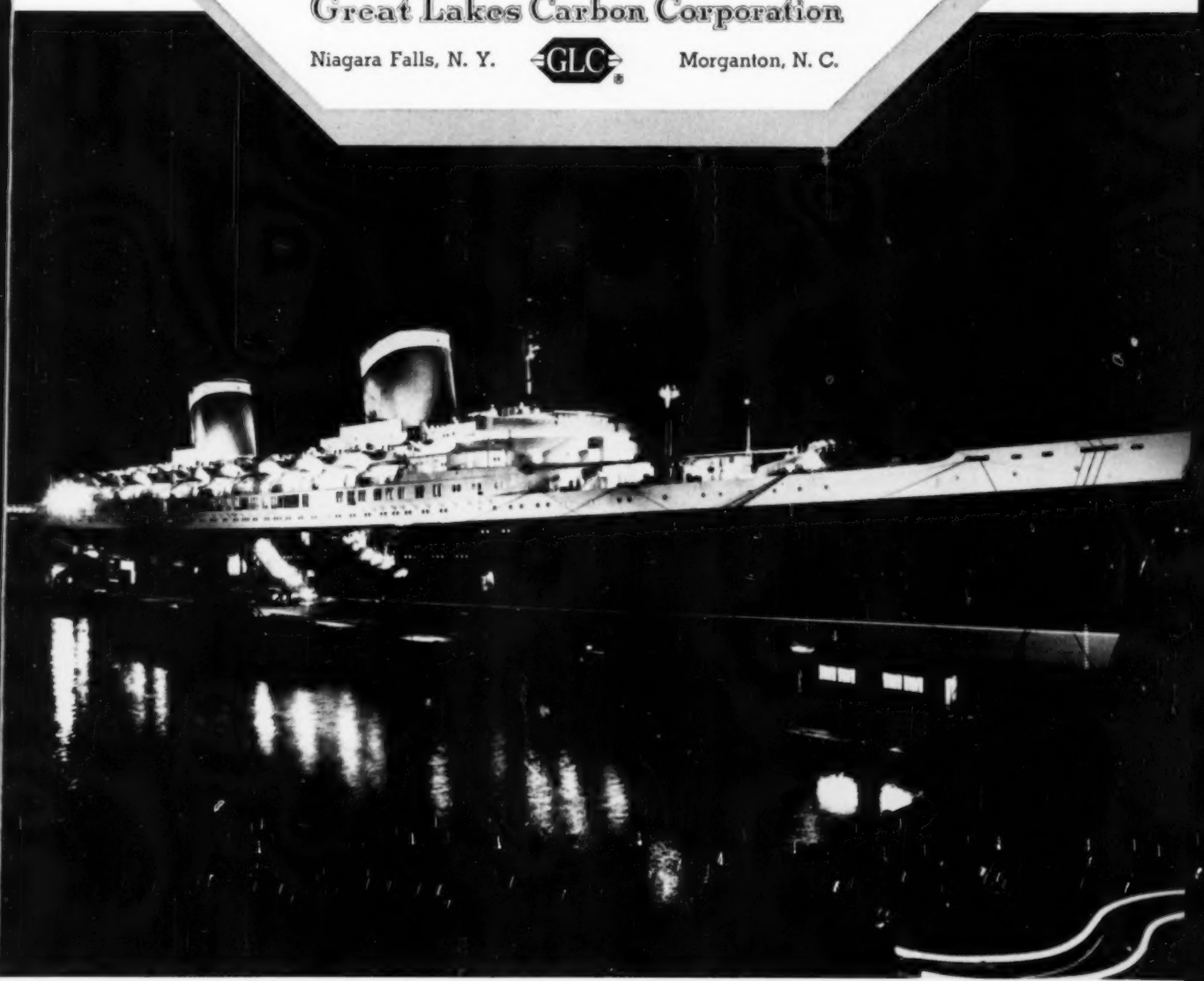

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METAL-CERAMIC METALLURGIST: Industrial research laboratory requires man to initiate programs on metal ceramics and related applications of powdered metallurgy; conduct independent investigations as well as direct group of technical men engaged in metal ceramic research. Fields covered will include development and evaluation of new types of metal ceramics and studies of fabrication techniques. Research may include fundamental studies on the nature of the bond and reasons for high temperature strength of metal ceramics. Please send outline of qualifications, personal background, and educational summary.

Box B-12 JOURNAL OF METALS

METALLURGICAL RESEARCH

The Armour Research Foundation of the Illinois Institute of Technology solicits employment inquiries from metallurgists interested in physical metallurgy, welding, powder metallurgy, foundry, and others. The requirements for current research and development openings cover a wide range of professional stature—from recent grads to mature research scientists. The Armour organization affords an unusual opportunity for continued professional development through pleasant associations with other metallurgists having mutual technical interests. Your inquiry will be confidential, and we will be pleased to respond with further information about current opportunities.

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ALUMINUM

FOIL METALLURGIST

Metallurgist experienced in foil production methods from ingot casting and rolling operations to finishing required by prominent aluminum producer. Excellent opportunity for thoroughly trained and experienced nonferrous man. Give complete information on age, education, experience, and salary required.

Box B-5 JOURNAL OF METALS

EXTRACTIVE METALLURGIST: 3 to 5 years' experience in various phases of mineral dressing desired. Some experience in magnetic separation would be helpful. Excellent opportunity in the less common elements. Send resume to:

Box B-6 JOURNAL OF METALS

PILOT PLANT DEVELOPMENT ENGINEER: Industrial research laboratory requires man to assume operating responsibility associated with chemical pilot plant development. Scope of engineering activity may involve design of apparatus to carry out a chemical operation, construction, and maintenance of such equipment, evaluation of the facility's efficiency, determination of required design alterations, and supervision of laboratory personnel. Please send outline of qualifications, personal background, and educational summary.

Box B-10 JOURNAL OF METALS

PHYSICAL CHEMIST: Conduct basic research in an industrial laboratory on the physical chemistry of liquid metals. Organize and execute program leading to practical improvements in methods and materials for the oxidation, desulphurization, etc. of steel and the solution of other problems encountered in the melting of steel and other metals. Please send outline of qualifications, personal background, and educational summary.

Box B-11 JOURNAL OF METALS

CORROSION CHEMIST: Industrial laboratory performing metallurgical research requires men to initiate and carry out fundamental inquiries pertinent to mechanisms of corrosion of metals in various corroding media. Develop testing techniques for investigating electrochemical phenomena which may be involved in the corrosion of various metals in different environments. Ultimate objective of research is the origination of new alloys with superior corrosion resistance and the development of treatments that will enhance the corrosion resistance of present materials. Please send outline of qualifications, personal background, and educational summary.

Box B-13 JOURNAL OF METALS

RESEARCH METALLURGICAL ENGINEER: Physical Metallurgist or Metallurgical Engineer with advance academic training and up to ten years' industrial experience wanted to head metallurgical research and development section in nonferrous field. Experience in field of powder metallurgy or refractory metals desirable. Salary commensurate with background and experience of applicant. Reply in confidence giving complete background to:

Box B-8 JOURNAL OF METALS

WANTED

Metallurgist with experience or training in nonferrous metallurgy. Powder metallurgy experience desirable but not essential. Work on research and development of special products in small community in northwestern Pennsylvania.

Box A-3 JOURNAL OF METALS

— Personnel Service —

THE following employment items are made available to AIME members on a nonprofit basis by the Engineering Societies Personnel Service, Inc., operating in cooperation with the Four Founder Societies. Local offices of the Personnel Service are at 8 W. 40th St., **New York 18;** 100 Farnsworth Ave., **Detroit;** 57 Post St., **San Francisco;** 84 E. Randolph St., **Chicago 1.** Applicants should address all mail to the proper key numbers in care of the New York office and include 6c in stamps for forwarding and returning application. The applicant agrees, if placed in a position by means of the Service, to pay the placement fee listed by the Service. AIME members may secure a weekly bulletin of positions available for $3.50 a quarter, $12 a year.

— POSITIONS OPEN —

Project Engineer, not over 50, for household appliance development. Must have minimum of five years' experience on processing of metal particularly sheet metal, and ability to carry through from inception. Salary, $8000 a year or better. Location, Wisconsin. Y8007CD.

Metallurgist to run a mill, with tin and tungsten experience. Salary, $8000 to $9000 a year. Location, Alaska. Y8004.

Junior Executives, experience in machine tool or heavy metalworking industry desirable. Will work closely with department head and with customers or suppliers in one of the following phases of the business: Contract terms, delivery dates, scheduling of machine installation and servicing repair parts. Purchasing and scheduling delivery of necessary electrical and hydraulic equipment initially, and later, patterns, rough materials and all other supplies; supervising the development of better electrical controls for general purpose machines; keeping up with new improvements and developments through close contact with electrical and hydraulic suppliers. Salary open. Location, northern Illinois. Y7984.

Metallurgists (a) Research metallurgist, 25 to 40, with experience in extrusion or similar operations and should have either a Master's degree plus 5 years' experience, or a B.S. degree plus 10 years' experience. Will be assigned as a project leader for certain alloy research work being done for the government. Salary $5876 to $7228 a year. (b) Research metallurgist, 25 to 40, with Master's degree in physical metallurgy or experience in industrial equipment. Will consider a young man with good metallurgy education but with no industrial experience. Salary, $5876 to $7228 a year for man with experience; $4160 to $4940 a year without experience. Location, Connecticut. Y7756.

Associate Metallurgist or Metallurgical Engineer, B.S. metallurgy, not over 30 for fabrication of nonferrous components for nuclear reactors through known techniques or special techniques or special techniques developed as needed for atomic energy. Must have had five years' experience on the use of vacuum techniques of melting and casting nonferrous alloys and small arc melting furnaces and induction furnaces. Must also have knowledge of nonferrous metal fabrication. Salary, $465 to $885 month. Location, Chicago. R9275(b).

Assistant Plant Superintendent with considerable experience in production of small metal goods items such as assembling, stamping, plating, polishing, etc. Salary to $7500 a year. Location, northern New Jersey. Y7733.

Mineral Dressing Engineer, mining or chemical, age to 35. Must have knowledge of flotation. Will do applied research and field evaluation on cationic and anionic flotation agents. Will be trained in flotation and eventually work into sales development and research. Salary to $7000 per year. Some traveling. Car required. Location, Chicago. R9232.

Welding Engineer, M.S. Met., M.E. or E.E., up to 35 years of age. Prefer two years' experience in welding research work but may consider qualified recent graduate. Must know ferrous metals and welding procedures. Work will be on research of welding projects for oil refinery. Salary, $5520 to $7200 a year. Location, Chicago. R9479(a).

Research Assistant, minimum requirement B.S. in metallurgy, chemistry or physics. Metallography, mechanical testing, statistical studies, interpretation of data, writing of technical reports and papers. Opportunity for tuition free advanced study and for publishing technical material. One month's vacation. Apply by letter giving qualifications and salary expected. Must be U. S. citizen. Location, western Pennsylvania. Y7172.

Engineers, graduates, with degrees in metallurgy or the equivalent in education and/or experience, e.g., chemical engineer, chemist, etc., for major producer of steel products. (a) Metallurgical trainee, $3912 a year. (b) Specification analyst, $4104 a year. (c) Metallurgists, $4392 a year. Automatic increases monthly for six months. Location, California. Y7798.

Chemical Engineer, young, with a metallurgical background and about two years' experience on corrosion problems for research and development work in this field. Salary, $5100 a year. Location, northern New Jersey. Y7496.

Research Assistant in metallurgy at eastern university. Post graduate work for Ph.D. degree. Selection of research problem in variety of fields, including welding, induction heating powder metallurgy, electrometallurgy and magnetic materials. Location, Pennsylvania. Y6330.

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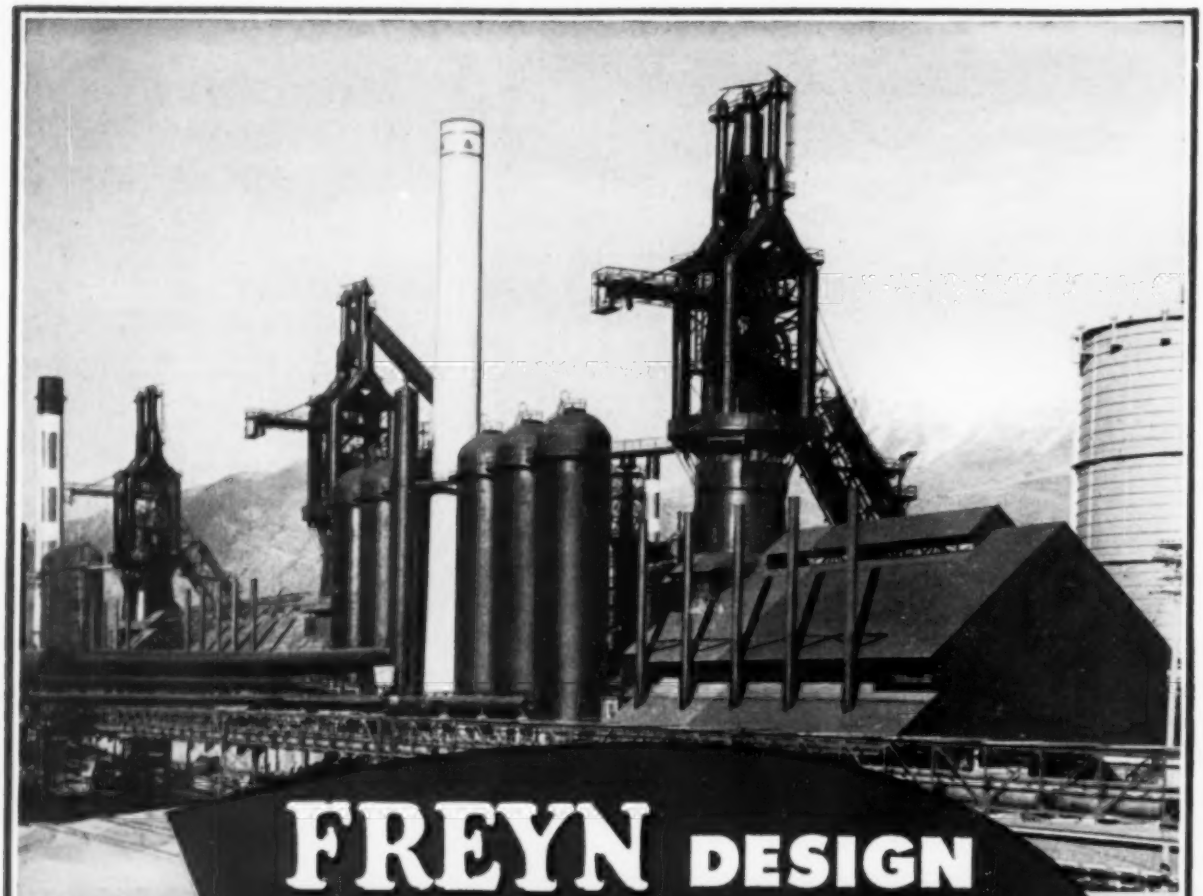
Box B-7 JOURNAL OF METALS

TECHNICAL ASSISTANT to Research Director. Must be graduate metallurgist with ability to write clear, concise reports interpreting research results. Background in ferrous metallurgy, welding, corrosion desirable. Chicago region, salary open. Reply in confidence to:

Box B-9 JOURNAL OF METALS



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Books for Engineers

Nonferrous Physical Metallurgy, by Robert J. Raudebaugh. *Pitman Publishing Corp.* $6.50, 334 pp., 1952.—The latest developments in the processing, fabrication, and application of 20 nonferrous metals and their more important alloys are summed up and clarified in this handy volume. Particular attention is given to currently important topics such as theory of age hardening, continuous and semicontinuous casting of ingots, arc melting of molybdenum, titanium and titanium alloys, cermets and ceremals, recrystallization studies of beryllium metal, and natural and radioactive isotopes. Important and recent findings reported by AIME, ASM, and the British Institute of Metals, as well as recent reports from industrial organizations are included. The book contains a comprehensive table of contents, subject and author indexes, and bibliographies for each chapter to make it a workable reference.

The Principles of Physical Metallurgy, by Gilbert E. Doan. *McGraw-Hill Book Co.* $5.50, 331 pp., 1952.—As in earlier editions, the author uses classical chemistry and physics to approach his subject. Beginning with the states of aggregation, he subsequently presents a coherent and organically unified account of the behavior of metals under the influence of metal fabricating and manufacturing industries operation. Basic principles of metallic behavior are stressed over the particular alloys or processes. However, the reader must know these alloys and learn the basic processes and problems involved in their use to fully understand their relation to fundamental principles. Thus, separate consideration of the commercial aspects of the major metals and alloys is given briefly.

Soluble Silicates, Vol. II, by James G. Vail. *Reinhold Publishing Corp.* $15.00, 669 pp., 1952.—The monograph has been divided into two parts to give the technician a rapid reference source. Vol. II, slightly larger than the first, deals with the practical considerations of soluble silicates to industry. Film forming properties of silicates and their uses in all manner of industrial materials and techniques including adhesives, laminates, sizing, fire protection, cements, and plastics are described. Use of soluble silicates in gel forms and their many valuable properties as catalysts, protective agents and stabilizing materials are covered in great detail. Both volumes place emphasis upon principles and properties rather than upon degree of industrial significance. Ideas are expressed in simple terms with a minimum of mathematical or highly specialized language.

Metal Data, second edition, by S. L. Hoyt. *Reinhold Publishing Corp.* $10.00, 526 pp., 1952.—The book, a new edition of the author's *Metals and Alloys Data Book,* contains the most recent information available and new data on such topics as hardenability of H-steels, recently developed super alloys for high-temperature stress members, and other new alloys. The purpose of the book was the selection of important data from reliable sources, and to present them in a form readily usable as a daily reference by metallurgists and engineers. Most of the material is presented in table form with a minimum of descriptive text. Nearly 700 tables and graphs give useful working information on such metallic properties as tensile strength, hardenability, thermal expansion, creep strength, endurance limit, and yield strength at normal, subnormal, and elevated temperatures, and for various conditions of mechanical treatment. Special features include listing of commonly used test bars, hardness tests, corrosion data, conversion factors, applications of materials, and the properties of elements.

Physical Metallurgy for Engineers, by Donald S. Clark and Wilbur R. Varney. *D. Van Nostrand Co., Inc.* $6.50, 567 pp., 1952.—A basic textbook for undergraduate engineering students, the book is intended to be correlated with design courses. Only the most elementary principles are presented to give the student an understanding of the materials with which he will deal. Ferrous and nonferrous metals are covered. Special properties, heat treatment, corrosion, casting, mechanical working, and joining methods are dealt with as well as basic metallurgy. Questions appear at the end of each chapter as a study aid.

Electronic Engineering Principles, by John D. Ryder. *Prentice-Hall, Inc.* $9.00, 505 pp., 1952.—The object of the book is to supply the physical fundamentals required for an understanding of electron tubes. The volume covers theories of conduction, simple atomic structure, and generalized circuit analysis with linear and nonlinear circuit elements. A basic knowledge of alternating current network theory and mathematics through simple differential equations is assumed. Physics involved in emission, space charge, and gaseous conduction phenomena is explained. Theory and applications are closely grouped. Applications have been chosen mainly from the industrial field. A new chapter on solid-state devices and the transistor has been added. Selected vacuum tube characteristic curves are appended.

High-Energy Particles, by Bruno Rossi. *Prentice-Hall, Inc.* $12.50, 569 pp., 1952.—The author has two objectives—to give a comprehensive account of present knowledge concerning high-energy phenomena, to describe its historical development, and to explain the research methods peculiar to the field; and to provide the active investigator with a report on current problems in high-energy physics and present him with a collection of formulas, tables, and graphs useful to his work. Cascade showers and the theory of electromagnetic interactions are dealt with in detail.

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Mass Spectrometry, Report of a Conference held in Manchester, England, 1950. *Institute of Petroleum.* 30s, 205 pp. 1952.—Instrumental aspects of mass spectrometry and its various applications in the study of the chemical reactivity of molecules, in isotope assay, in biochemistry, and in gas analysis are discussed. The preparation of standard gases necessary in calibrating the mass spectrometer is also included. References are given at the end of each chapter and an extensive bibliography on the spectrometer is listed.

Atomic Power, by Walter Isard and Vincent Whitney. *Blakiston Co.* $4.75, 235 pp., 1952.—Beginning with a brief resume of the technical background, the authors continue with a factual analysis of the economic, sociological, political, and geographical aspects of atomic power development. Part II deals with costs and industrial applications, utilizing the iron and steel industry and the aluminum industry as case studies. Part III discusses the relation of atomic power to the process of economic development and its impact upon regional economies, with Brazil particularly considered as a case study.

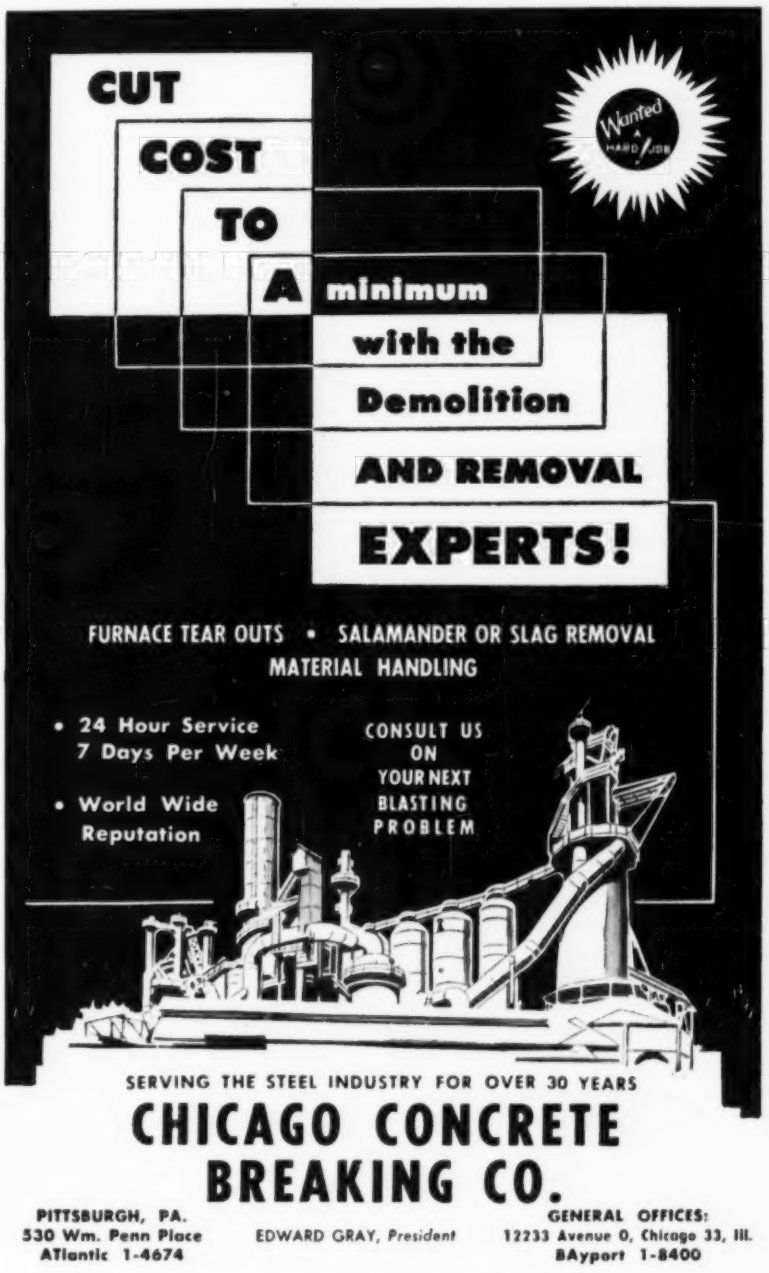
Advances in Electronics, Vol. IV, edited by L. Marton. *Academic Press, Inc.* $7.80, 344 pp., 1952.—An up-to-date review of outstanding developments in the field both in the United States and abroad is presented. Each chapter summarizes important progress in theory, techniques, and devices made in the past year. Some of the chapter headings are: Electron scattering in solids; electronic digital computers; magnetic air-borne detector; and scintillation counter. Reference lists follow each chapter.

Story of the Mushets, by Fred M. Osborn. *Thomas Nelson & Sons, Ltd.* 21s, 195 pp. 1952.—This book tells the story of Robert Mushet and his father, David Mushet — 19th century pioneers in the development of the iron and steel industry. The narrative centers upon Robert Mushet's contribution in making the Bessemer process practicable for the production of cheap steel, and his discovery of self hardening tool steel. Appendices give a list of patents obtained by both father and son. A considerable selection of the original correspondence concerning the Bessemer process and other matters are included.

Advanced Strength of Materials, by J. P. Den Hartog. *McGraw-Hill Book Co., Inc.* $8.50, 379 pp., 1952.—Starting from the level attained in most first one-term courses in engineering colleges, the volume covers the following major subject headings: Torsion; rotating disks; membrane stresses in shells; bending of flat plates; beams on elastic foundation; two-dimensional theory of elasticity; the energy method; buckling; miscellaneous topics such as Mohr's circle and certain specialized theorems.

Atlas Metallographicus Ternare Legierungen des Aluminiums, Vol. III, Part 2, by Heinrich Hanemann and Angelica Schrader. *Verlag Stahleisen M. B. H.* Dusseldorf. $6.40, 280 pp., 1952.—The book summarizes data from the literature on 37 ternary systems of aluminum and presents the results of extensive experimental work by the authors on those systems. The book contains 502 good photomicrograph reproductions. Data is clearly, concisely, and systematically presented. The book, well written, is aimed at metallographers who work with aluminum alloys.

Willis Haviland Carrier, Father of Air Conditioning, by Margaret Ingels. *Country Life Press.* $2.50, 170 pp., 1952.—While depicting the life of Willis Haviland Carrier, the book is also the story of the company he founded and the industry in which he pioneered. The book contains a chronological table, covering the years 1500 to 1952, showing the development of air conditioning. Written in nontechnical language, the book covers the boyhood, education, business and trials of Carrier.



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Industrial Notes . .

• Research is expected to play an important role in the 1953 plans of the Dravo Corp. New consolidated facilities under construction at Neville Island will be administrated by a newly created department. One of the projects under way, although laboratory construction has not been completed, is a study of protective coatings for ferrous metals.

• **Contract to rebuild three coke oven batteries at U. S. Steel's Clairton works has been awarded to the Koppers Co., Inc. The batteries will contain 64 ovens each. Coking capacity of the plant will be increased an estimated 800 tons per day, with each battery carbonizing 1280 tons of coal daily. Three other batteries being rebuilt by Koppers at Clairton are expected to be back in operation early this year.**

• Recent allocation of the Federal Communications Commission of 70 new TV channels in the ultra-high frequencies has prompted General Electric Co. to double production of germanium anodes. Tuners and converters to permit UHF reception require one or more germanium anodes. Production has been increased gradually at the company's Clyde plant. Automatic and semiautomatic machines coupled with slightly increased employment has made the production hike possible.

• *Ben Moreell, chairman of the board of Jones & Laughlin Steel Corp. announced J&L expects to complete the following projects this year: A new bar mill, a battery of 79 byproduct coke ovens, increased storage areas, and parking facilities in the Hazelwood expansion in Pittsburgh; electrification of the steam-driven blooming mill at Aliquippa; development of J&L Tracy mine, deep shaft iron ore mine in northern Michigan; three additional diesel towboats for the river transportation div.; improvement of the 14-in. hot rolling mill at Aliquippa; and modernization of the limestone quarries in W. Va.*

• The Meehanite Metal Corp., New Rochelle, N. Y. is now installed in a building purchased at 714 North Ave., New Rochelle. In addition to office facilities, the building includes enlarged laboratories for experimental melting, chemical and physical testing, and photomicrographic studies.

• *Westinghouse Electric Corp. will build the first welding electrode plant in the south near Montevallo, 38 miles south of*

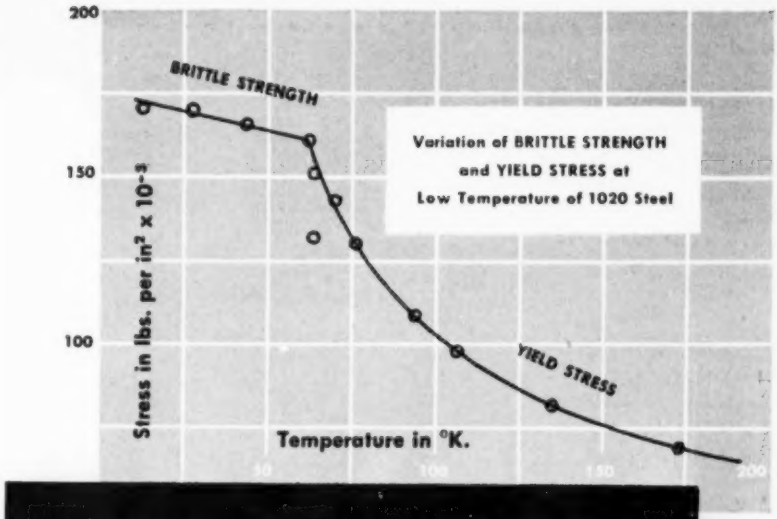
Birmingham, Ala. Its principal product, welding electrode, will supply all of the South and Pacific Coast states, while brazing alloys manufactured will be shipped throughout the U. S. Plans call for a one-story brick structure more than 400 ft long. It will be part of Westinghouse's $296 million expansion program.

• Another step was taken toward centralizing the division of Beckman Instruments Inc., with the approval of the Orange County, Calif., Planning Commission to change the new Beckman site from suburban residential to manufacturing. An office building, an assembly building, a warehouse, and machine shop will be erected on the new site. Presently, Beckman occupies 16 separate buildings at their South Pasadena location.

• **Ohio Ferro-Alloys Corp., of Canton, Ohio has been appointed exclusive sales representative to the iron and steel industry for Cerium Metals Corp., of New York City. The Canton firm will represent Cerium through their sales and service staffs in Chicago, Detroit, Pittsburgh, Tacoma, Seattle, Los Angeles, San Francisco, Birmingham, Minneapolis, and Canton. Cerium products to be sold are mischmetal, cerium and rare earth alloys, and cerium master alloys containing aluminum, magnesium, manganese, silicon and other elements.**

• All assets and manufacturing rights of the Bridgeport Safety Emery Wheel Co., Inc., of Bridgeport, Conn., and the Diamond Machine Co., of Stratford, Conn., have been acquired by Columbia Machinery & Engineering Corp. Purchase was reportedly for cash. Columbia plans to integrate the two companies with its Hamilton, Ohio plant at least temporarily. Columbia intends to continue manufacturing Bridgeport's full line. For the present, its connection with the Diamond Co. will be limited to field service.

• American Messer Corp. has become the first American firm to affiliate with a German company since the end of World War II, under a new law passed by the Bonn Government making the alliance possible. American Messer is affiliated with Adolf Messer, G.m.b.H. Frankfort, manufacturer of oxygen and nitrogen plants and welding equipment. The 50-year old German firm was active in the U. S. prior to the war. A recent Messer development is a process for producing argon from air.



1020 Steel at 61.5°K.

A need for measurements of brittle strength as a function of temperature prompted the results shown in the curve above. Several samples of hot-rolled 1020 steel were tested at various temperatures in the interval 12°K. to 61.5°K. All exhibited brittle fracture with no reduction in area. At 75°K., however, a definite yield point was observed and the increase in length before rupture was unexpectedly large. Several additional specimens were broken at temperatures lying between 61.5° and 75°K. The results indicate a sharp transition near 61.5°K., below which no reduction of area occurs and above which the reduction of area increases rapidly as the temperature at which the sample is broken rises above 61.5°.

The ADL Collins Liquid Helium Cryostat, by providing test chamber temperatures from ambient to —271°C., makes many research projects like this possible. Superconductivity, resistance minima in metals at low temperature, and thermal conductivity are a few of the studies utilizing the ADL Collins Cryostat, the basic tool of a new research frontier.

For further information request Bulletin JM 9-3 including details of the Collins Helium Cryostat and a reprint of "Fracture and Yield Stress of 1020 Steel at Low Temperatures" by A. S. Eldin and S. C. Collins.

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ELECTROMET Data Sheet

A Digest of the Production, Properties, and Uses of Steels and Other Metals

Published by Electro Metallurgical Company, a Division of Union Carbide and Carbon Corporation, 30 East 42nd Street, New York 17, N. Y. • In Canada: Electro Metallurgical Company of Canada, Limited, Welland, Ontario

Deoxidation Studies Show Advantages of Silicomanganese

Silicomanganese has proved to be highly efficient and economical as a furnace block and deoxidizer, as well as an alloy addition. Steel producers have found that it saves furnace time, produces cleaner steel, and increases the yield of rolled products.

Excellent Blocking Addition

When used as a blocking addition, silicomanganese stops the carbon-oxygen reaction in the open-hearth furnace and permits close control of analysis. The alloy has a ratio of approximately 3.5 manganese to 1 silicon. This proportion will produce a high degree of deoxidation in the furnace.

Why Silicomanganese Is Effective

The carbon boil is arrested more positively by this combination alloy, containing both silicon and manganese, than it is by larger amounts of silicon alone. As a result, close control of the carbon level can be maintained. Also, because of the low carbon content of silicomanganese, the heat may be blocked at a comparatively high carbon level. This saves furnace time, which is critical in reducing costs. Since silicomanganese gets more oxygen out of the bath than silicon alone, the steel is cleaner and has improved surface quality.

Metallurgical Studies Made

Work done by Herty and his associates (1) showed that manganese tends to flux silica inclusions resulting from deoxidation, and permits them to grow in size so that they float out of the bath more rapidly.

More recently, it was found by Hilty and Crafts (2) that manganese and silicon in combination lower the oxygen content much more than silicon alone (see Fig. 1). They also determined that, although manganese by itself is not a strong deoxidizer, it substantially intensifies the deoxidizing power of silicon.

It was shown that in steels with lower silicon contents (below 0.05 per cent), manganese in the amounts usually present as a residual has a strong influence. However, in the silicon range normally used for deoxidation (0.05 to 0.25 per cent), more manganese is required to obtain the full benefit of the combined deoxidizers. For example, at 1600 deg. C, iron with 0.10 per cent silicon and 0.10 per cent or less manganese contains about 0.017 per cent oxygen. With 0.50 per cent manganese, it contains only 0.009 per cent oxygen (see Fig. 1).

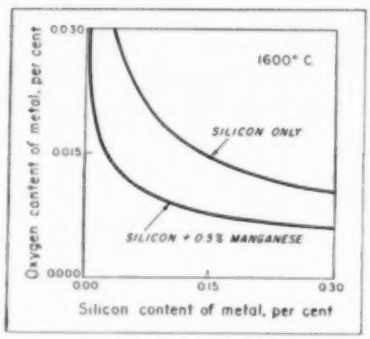

Fig. 1. Limit of solubility of oxygen in iron-silicon alloys, plain and with 0.50 per cent manganese at 1600 deg. Centigrade.

These data thus confirm an observation made by Tenenbaum and Brown (3) that steel as tapped from the furnace is materially lower in oxygen after blocking with silicomanganese.

In another study, made by Silliman and Forsyth (4) it was demonstrated that heavier than usual additions of silicomanganese result in a marked improvement in surface quality. About twice the usual addition of silicomanganese gives a substantial increase in the yield of finished product.

Silicomanganese Produces Cleaner Steel

Initial deoxidation in the furnace with silicomanganese produces very clean steel, particularly in grades below 0.25 per cent carbon. Several factors contribute to the cleansing action of silicomanganese. The amount of dirt in steel seems to be proportional to the maximum oxygen content prior to final deoxidation. Heats that are oxidized to a low carbon and recarburized, as were early rail and forging steels, are dirtier than those in which the carbon is "caught on the way down."

It is also well recognized that medium-manganese and low-carbon steels that are blocked at higher carbon (lower oxygen) contents, with low-carbon ferro-alloys, are cleaner than those taken to a lower carbon level and recarburized with high-carbon ferro-alloys. Silicomanganese is low enough in carbon to block at higher carbon levels. As pointed out by Tenenbaum (5), there is also a decided economic advantage in not driving to such low carbon contents before blocking.

Suitable For Ladle Additions

In addition to its use as a bath deoxidizer, silicomanganese has proved particularly effective as a ladle addition for the deoxidation of semi-killed steels. The alloy is also used to provide the complete ladle addition of manganese in the manufacture of medium-manganese, acid-steel castings.

Metallurgical Service Available

Our metallurgists will be glad to help you with the use of ELECTROMET silicomanganese. This alloy contains 65 to 68 per cent manganese, and is produced in maximum 1.50, 2.00, and 3.00 per cent carbon grades. All grades are furnished in a lump size of 75 lb. x 2 in. and in a crushed size of 2 in. x down. If you wish further information, please write, wire, or phone the nearest ELECTROMET office: in Birmingham, Chicago, Cleveland, Detroit, Houston, Los Angeles, New York, Pittsburgh, or San Francisco. In Canada: Welland, Ontario.

References

1. C. H. Herty, Jr., C. F. Christopher, M. W. Lightner, and H. Freeman: "The Physical Chemistry of Steelmaking; Deoxidation of Open-hearth Steel with Manganese-silicon Alloys." U. S. Bur. of Mines, Carnegie Tech. and Min. and Met. Advisory Boards, Coop. Bul. 58, 1932.
2. D. C. Hilty and W. Crafts, "The Solubility of Oxygen in Liquid Iron Containing Silicon and Manganese," Trans. AIME, 188, 1950, pp. 425-436.
3. M. Tenenbaum and C. C. Brown, "The Total Oxygen Content of Plain Carbon Open-hearth Steel During Deoxidation and Teeming," AIME 162, 685-703, 1945.
4. L. R. Silliman and H. F. Forsyth, "Deoxidation vs. Surface Quality," Open-hearth Proceedings, 32, 1949, pp. 218-224.
5. M. Tenenbaum, "The Economic Aspects of Deoxidation," Open-hearth Proceedings, 28, 1945, pp. 349-352.

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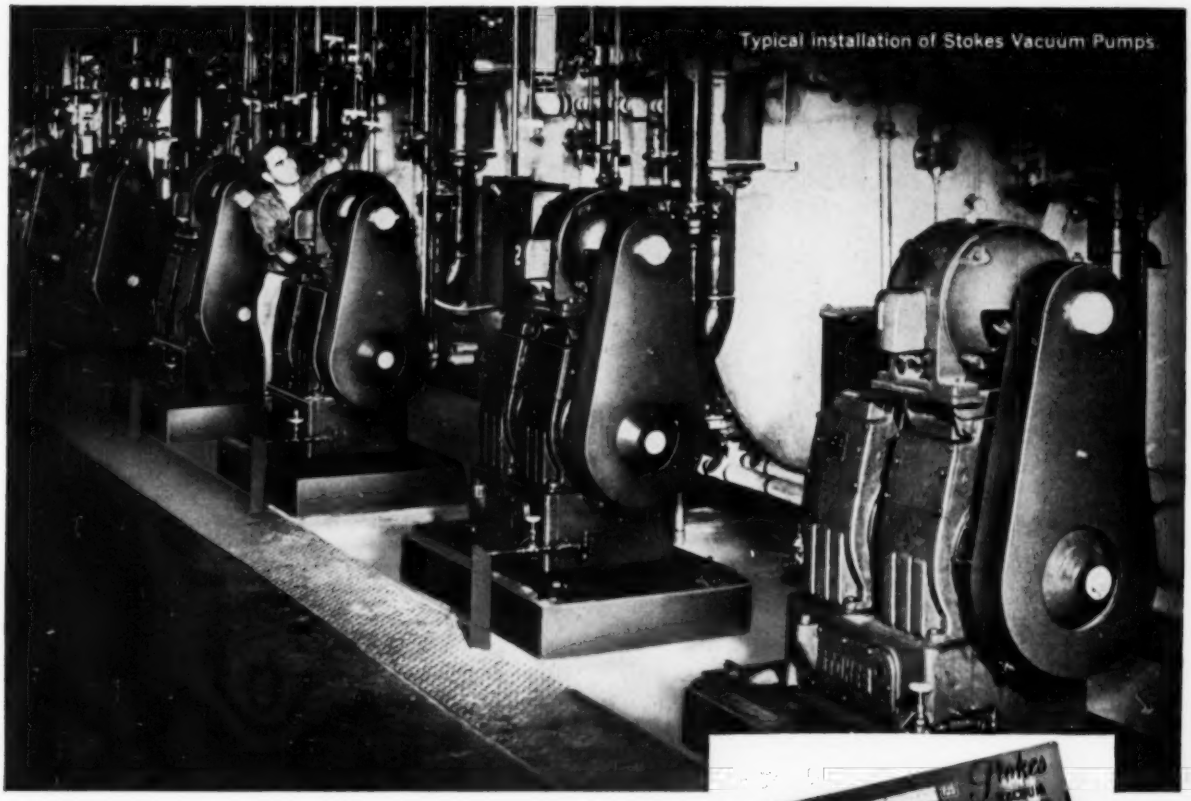

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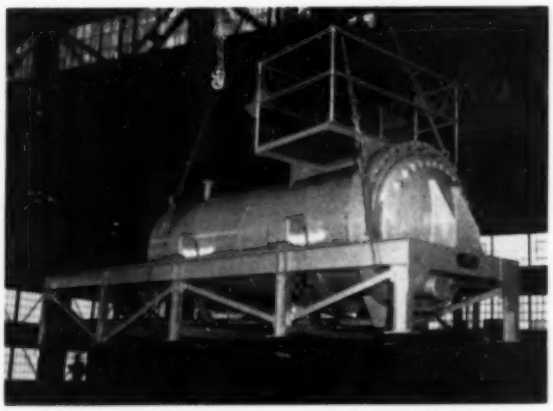
Journal of Metals

FREE world production of nickel approximated 315 million lb in 1952, according to John F. Thompson, chairman of the board of International Nickel Co., with Canada producing about 90 pct of the total. Free world production was estimated at about five times that of the rest of the world. Thompson voiced the opinion that the nickel situation is still not healthy enough to supply large government stockpile requirements simultaneously with unrestricted use in the civilian economy and defense programs. However, nickel allocations made by the International Materials Conference have been in excess of defense requirements and nickel has been available for civilian consumption to some extent.

Much has yet to be accomplished before a satisfactory state is reached. Exploration is going on at an unprecedented rate, with several new companies involved. Most of the work is being financed by private capital, Thompson said. Some of it, however, is financed by the U. S. and other governments. Inco, Falconbridge Nickel Mines, Ltd., Sherrit Gordon Mines, Ltd., Nicaro, and the French firm of S. A. Le Nickel have been engaged in expansion programs.

International Nickel, world's largest nickel producer, is pushing toward completion of its $150 million program. The company financed program will be finished sometime in 1953 according to Thompson. It is expected to give Inco a 13 million ton annual ore capacity entirely from underground operations. Thompson noted that this would insure Inco's current production of 250 million lb of nickel per year. Thompson said that Falconbridge, Canada's second largest producer is engaged in a program which reportedly will give the firm an annual capacity of 35 million lb by 1954. The U. S. government financed Nicaro nickel project in Cuba is reported nearing its goal of 30 million lb of nickel annually, according to Thompson. Sherrit Gordon, developing a nickel-copper deposit at Lynn Lake, Manitoba, is constructing a 17-million lb annual capacity refinery scheduled for completion in 1953, Thompson said. The French firm S. A. Le Nickel, operating in New Caledonia is currently modernizing its operations while already producing 14 million lb annually, Thompson stated.



Retractable shell type pressure filter manufactured by Dravo Corp.'s Pittsburgh unit will be one of 24 used in a new basic aluminum plant. Developed by H. W. North Co., filters are for use in metallurgical and chemical industries for pressure filtration. The shell is 14 ft long and 60 in. diam, and is retracted by a screw mechanism. Remote control breech locks stationary unit head.

Largest users of nickel continue to be the U. S., the United Kingdom, and Canada, mainly for engineering steels, stainless steels, and jet alloys. The plating industry has been hit hard by government restrictions on civilian use. Even in cases where platers have been allowed to use nickel moderately, the thin coatings which have resulted have been far from satisfactory. No good substitute has been found. Industrial uses of nickel-plating under direct authorization through defense contracts have advanced because of the expanded use of heavy nickel deposits in place of solid and clad nickel.

In heat and corrosion resistant alloy castings nickel was allowed for industrial applications requiring high resistance to corrosion and strength at elevated temperatures. These alloys were used in many jet engine parts.

Worker at the Akron plant of Firestone Tire & Rubber Co., forms a stainless steel tail cone used to control exhaust gas discharge from the J-47 jet engine. Firestone has been manufacturing turbine casings, inner and outer combustion chambers, and exhaust cone assemblies.

COMMERCIAL taconite production, discussed endlessly in technical journals, seminars, and on panels, may be a reality by 1955 as the result of a $148 million loan made to Reserve Mining Co. Borrowed privately from major life insurance companies, the money will go into plant construction at Babbit and Beaver Bay, Minn. Total cost of the project has been estimated at about $160 million. Reserve's taconite deposits cover about 10,000 acres near Babbit. Remainder of the financing is expected to come from Republic Steel Corp. and Armco Steel Corp., joint owners of Reserve.

Content of the ore concentrate to be shipped is expected to run more than 60 pct iron, higher than the percentage customarily shipped from the Mesabi Range. The plant will include the world's largest crusher, a machine towering four-stories and whose

construction will take more than two years. Entire construction of the plant is scheduled for completion by June 1957, but ore shipments may leave Beaver Bay by 1955. The project will include an interplant railroad, a secondary crushing plant, a harbor, docks, ore boat loading equipment, and a 55,000 kw power plant located at Beaver Bay on Lake Superior. Also to be constructed are schools, dwellings and community buildings.

◆◆◆◆◆◆

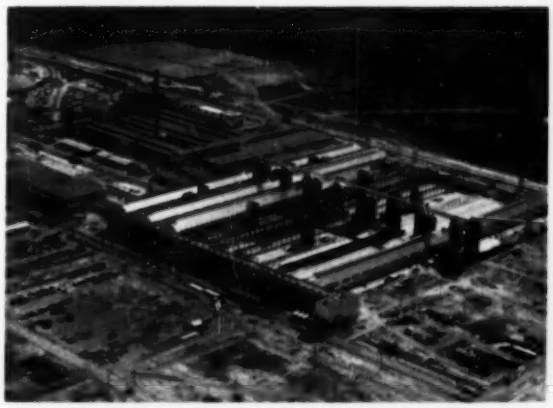
A NEW city of Pittsburgh, a city of clean air and clean buildings, is emerging. Slowly, its skyline is changing as old buildings are torn down to make room for new modern, functional structures. One of the most unusual, and perhaps the herald for a new era in American construction, is the home office of Aluminum Co. of America at Sixth Ave. and William Penn Way. The aluminum clad building rises 30 stories and has been described as *one big showcase of aluminum*. The building's walls, roof, ceilings, doors, hardware, baseboards, lathing, lobby trim, window-framing, waterpipes, electric wiring, and air conduits are made of aluminum. The building is an enormous test laboratory for the metal, proving its multitude of uses in architecture.

Currently, about 20 pct of U. S. aluminum production goes into building materials, but Alcoa hopes that the building will lead to an ever increasing use of the metal. Much experimentation went into the successful use of aluminum for the building. The chances are that the knowledge gained through actual experience would permit the building to be duplicated for much less than Alcoa spent on its construction.

One of the standout advantages claimed by the owners is that the building exterior is just about maintenance-free for life. The electrochemical finish on its outer panels give them a permanent slate gray color and what is called a self-washing quality. Heavy rain will clean them, it is said.

Radiant cooling and heating is obtained by use of aluminum ceiling panels backed by aluminum water pipes which carry hot or cold water as needed. The panels are perforated for acoustical treatment and backed by a fiber glass blanket. Mounted by hooking over the pipe gridwork, the panels are covered with heat absorbing paint. Even the water tanks mounted on the roof are of aluminum.

Use of aluminum does not mean that steel is completely absent from construction. About 6500 tons of steel went into the building—about half the amount usually required in buildings with comparable 300,000 sq ft of office space above the first floor. Many of the innovations in the building are not ready for commercial use. Plumbing is still being tested and developed, and door facings have proved too thin. Desks and other furniture have left almost irrepairable dents in the door facings. Aluminum electrical wiring has proven somewhat troublesome in the smaller sizes, but Alcoa is ready to tackle any building wiring job right now.



The second big Texas plant of the Aluminum Co. of America is nearing completion at Rockdale. It is expected to have a capacity of 85,000 tons of aluminum per year. Bethlehem Steel Co. fabricated and erected 11,000 tons of steel for the plant buildings.

Sacrificial pipe joints, a foot or more in length are being used to combat electrolytic corrosion, which attacks aluminum piping wherever it is attached to copper or similar metals. The sacrificial joints fit between the Alcoa building's own aluminum piping and the pipes on standard plumbing fixtures. The joints are of almost pure aluminum and attract electrolytic current away from other pipes and isolate the corrosion within themselves. Sacrificial pipes are located throughout the building and can be easily replaced as needed, although they are expected to last from 10 to 15 years.

◆◆◆◆◆◆

IF the price level can be protected, American lead mine operators can look forward to a satisfactory year in 1953, according to Andrew Fletcher, president of St. Joseph Lead Co. However, he termed as "inept" Government efforts in 1952 to stabilize the market for an international commodity. He pointed out that the Government had created an artificial shortage of the metal at the outbreak of the Korean war by establishing ceiling prices for lead and zinc, a procedure not followed by other countries. Lead, meanwhile, according to the St. Joseph president, and President of AIME for 1953, accumulated in European markets. When Great Britain sold some 60,000 tons of lead from her surplus to the U. S. for stockpiling, and the advent of the free offering of lead with the opening of the London Metal Exchange in 1952, the foreign price dropped to about 10¢ a lb and U. S. market declined from 16¢ to 13.50¢.

When the foreign market improved in December, some advance in the U. S. price was noted. U. S. consumption of lead in 1952 reached approximately 12 million tons. Domestic production reached 375,000 tons, a slight drop from the mark reached in 1951. Imports increased sharply to 535,000 tons, more than double the 258,000 tons in 1951. Scrap reclamation declined somewhat to 440,000 tons.

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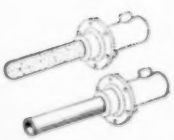

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H HONEYWELL

Drift of Things

WHEN asked a few weeks ago if we wished to visit the Coors plant at Golden, Colo., we agreed with alacrity being well acquainted with the high quality of Coors beer and having heard that the company was most liberal about sampling privileges. Instead of a brewery, we found ourselves in a pottery, the Coors Porcelain Co., owned and operated by the firm of beer fame. Our apparent disappointment was dispelled as the wonders of the porcelain products were unfolded.

Until this visit we had always thought of porcelain as fragile, used for bathroom vessels, dental fillings, or tableware; instead we found a whole variety of uses where metals had left off and ceramics had taken over. Our guide hefted a 2½ in. diam porcelain ball in his hand and then threw it on the floor catching it on the return bounce; the ball was not even chipped. Depending on the composition of the porcelain (alumina is a basic ingredient) products can be made with tensile strength up to 27,000 psi, compressive strength 290,000 psi, modulus of rupture 50,000 psi, modulus of elasticity 40,200,000 psi. In the extra-high strength ceramic a specific gravity of 3.57 and hardness of 9+ is attained. Products made from it are nonporous and refractory. For instance at 800°C the thermal conductivity is 29 Btu per hr per sq ft per °Fahrenheit per in.; the thermal coefficient of expansion between 25° and 1000°F averaging 9.14x10⁻⁶ per °C. Working temperature in the extra high strength ceramic is quoted at 1700°C maximum. Generally speaking this alumina porcelain is resistant to abrasion and corrosion even at high temperatures, is nonporous, and has a high dielectric constant.

Except for the grinding balls which come either in round or natural shape and are used for grinding in the paint, porcelain enameling, ceramics, and cement industries, the other products are designed to order. Such products as pipe and pump liners, bearing sleeves, and high refractory jet engine parts are made to name a few. The property of long-wear coupled with strength under high temperature or corrosive chemical conditions offers a multitude of possibilities for use.

Each order usually requires a tailor-made production setup. Since the porcelain cannot be machined to the close tolerances of steel, these limitations must be established. A mold is made for a basic shape from which the final product shape may be machined. In production, the porcelain powder compound is placed in a mold and subjected to high pressures; no heat is applied at this stage. The basic form is then put on a lathe, held by a vacuum chuck, and machined to specification. The raw product is then fired at about 2900°F. Thin structures, or those with sharp corners, can of course be chipped.

This type of porcelain manufacture stems from the spark plug manufacturers. The basic clay compound used is a craft secret. Those working with the high-density alumina ceramic are finding new and surprising uses as manufacturers send in their problems. Our only suggestion to date has been high density porcelain nursing bottles.

SIMULTANEOUS retirement of two respected leaders of the copper producing industry was an unusual coincidence. Louis Buchman and Burr Wheeler, vice-presidents, respectively, of Kennecott Copper and Chile Exploration Co., have more in common than the absence of a middle initial. Each has been directly in charge of operation of one of the two largest copper mines in the world; Mr. Buchman at the renowned Bingham pit of Utah Copper and Mr. Wheeler at the fabulous Chuquicamata pit in Chile. Both men started early with their respective companies and served continuously at the mining property which they later managed.

COMFORTING news has been received from the United Nations. The world has enough iron ore reserves to make 84 billion net tons of iron, which is computed to be enough to last 825 years at the current rate of consumption. On the same basis the report discloses 1.1 billion tons of manganese (50 pct Mn), enough for 250 years; 6.6 million tons of recoverable tin, 38 years supply; and chromite and tungsten in sufficient quantity for 47 and 125 years, respectively. On the all-important question of distribution the report points out that 47 pct of the iron ore reserves, 5 pct of the manganese, and 8 pct of the tin are in the Western Hemisphere. Nothing of course about company reserves distribution.

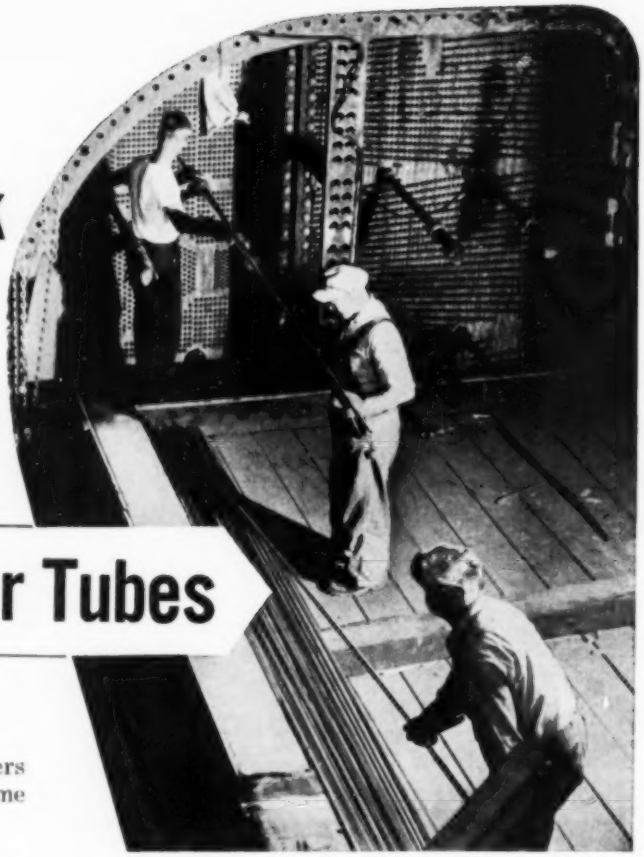
We imparted this information to Frank Sisco on the elevator and he took his pipe out of his mouth long enough to remark: "things haven't changed a bit I see, still arguing over resources." He went on to point out how nebulous reserve estimates on such a large scale were, expanding and contracting depending on who does the figuring.

This is not the first time the United Nations has shown an interest in world resource problems. In August 1949 a world resource conference at UN headquarters, then at Lake Success, gathered some of the world's leading scientists and engineers. In one particular session, which like the others was a melting pot of nations, the prodigality of the human race towards its natural resources became the paramount issue. A United States delegate deplored some of the extravagances of our high standard of living. This was greeted by approval from some of the Socialistic nations. When the Chairman of the meeting asked the U. S. delegate if he would recommend conservation in consumption, a rather delicate situation was created. The U. S. delegate, no doubt thinking of the bureaucratic ramifications of such a proposal, thought not.

On this particular day one Paul Foote, Gulf Research & Development Corp., supplied the answer which we like to use whenever the occasion arises. Speaking up boldly like a sturdy son of the free enterprise system he said in effect: "I will live prodigally, if that is what you call it, having confidence in the ingenuity of my fellow engineers and scientists to supply new ways of doing things with new materials as the old ones are exhausted."

John V. Beall

One Way to Lick Corrosion and Wear of Heat Exchanger Tubes



Anaconda 70-30 Cupro-Nickel Tubes, produced by AMERICAN BRASS COMPANY, Waterbury, Conn., were used to replace tubing of Admiralty Metal at the Harbor Steam Plant, Dept. of Water and Power, City of Los Angeles, Calif. View shows men retubing part of a 70,000 sq. ft. surface twin-condenser with 5,878 Anaconda cupro-nickel tubes ⅞" O.D. x 26' 3" long, serving a 75,000 KW turbine.

It takes a lot of handling to retube heat exchangers . . . and while the job goes on, equipment downtime plays mischief with production.

Minimize the risk of such shutdowns. Wherever heat-transfer capacity is a factor, especially where wall thickness of tubes allows but little tolerance for effects of corrosion and erosion, specify 70-30 cupro-nickel tubes.

Thin walls of this strong tough alloy resist corrosive and erosive attacks from all sorts of cooling media including polluted, silt-laden harbor water.

Along with ability to withstand a wide variety of corrosive agents, the 70-30 cupro-nickel tubing provides outstanding resistance to pitting and stress corrosion cracking.

* * *

Aship or ashore, this alloy gives unsurpassed performance in vital parts of equipment exposed to salt water corrosion.

In power generator stations, sugar mills, oil refineries and similar plants . . . cupro-nickel alloys serve in feed water heaters, condensers, evaporators and other heat exchangers, and in oil coolers, stills, water boxes, piping, tanks, and other equipment. Cupro-nickel alloys minimize maintenance and replacement expense, loss of heat transfer capacity and interruptions of operation resulting from corrosion.

Cupro-nickel is produced in tubing, rod, strip, wire and sheet, and also in cast form. We shall be glad to give you additional information and help you select the one best suited to your requirements. Write us today.

At the present time, nickel is available for the production of cupro-nickel and other alloys containing nickel, for end uses in defense and defense supporting industries. The remainder of the supply is available for some civilian applications and governmental stockpiling.

THE INTERNATIONAL NICKEL COMPANY, INC. 67 WALL STREET NEW YORK 5, N. Y.

An Export-Import Bank loan of up to $67.5 million has been approved for Industria e Comercio de Minerios, S.A., (Icomi) of Rio de Janeiro for production of high grade manganese ore from new Brazilian deposits. Under terms of a DMPA contract, the U. S. will get at least 70 pct of the 5.5 million tons of ore to be produced over a period of several years. Bethlehem Steel Co. holds a partial interest in the Brazilian firm. Large scale production is expected by 1956 with the company to deliver 400,000 tons of ore during that and the following year. The ore is said to average 45 to 47 pct manganese.

Plans for a 75 pct increase in capacity of the Government owned Nicaro nickel plant in Cuba, were announced by Jess Larson, Defense Procurement Administrator, who leaves with the outgoing administration. Built during World War II, the plant was reopened in 1952 with annual production goal of 30 million lb of nickel. Larson also hinted at possible expansion of Canadian nickel production.

Steel capacity of the U. S. increased 8,959,800 tons a year in 1952. The gain was almost 2 million tons more than expected and was the largest gain in capacity ever made in a single year. It increased the industry's annual capacity to a record 117,547,470 net tons annually. New weekly capacity figure, basis for the industry's weekly operating rate, is 2,254,459 net tons of ingots and steel for casting. The old rate, used in 1952, was 2,077,040 net tons.

Chrome shipments from Southern Rhodesia are being bottlenecked in transit from mine to port by a one track railroad. However, a loan of up to $14 million granted near the old ECA in 1951 will be available for line improvement sometime this year. The U. S. gets most of its chrome from Southern Rhodesia and Turkey.

Canada's first refinery for the production of pure tungsten carbide from tungsten ores was announced by Kennametal, Inc. The new plant, known as Macro Div. of Kennametal, Inc., is located at Port Coquitlam, British Columbia. In addition to tungsten carbide, the new plant will produce titanium carbide.

Bethlehem Steel Co. started pouring steel for the 50,000-ton die forging press being constructed under the Air Force heavy press program. A new mold, 18 ft tall and 9 ft in diam, was used to cast the first steel for the column forgings. Each rectangular column will be fabricated of three rectangular forgings up to 110 ft long. The press will stand 10 stories high when finished. A 100-ft deep foundation has been constructed at North Grafton, Mass., where Loewy Construction Co., of New York is building the press for Wyman Gordon.

A million dollar pilot plant for the recovery of manganese from steel slag at Coxton Yards, Pittston, Pa., came nearer to reality with the application for a Certificate of Authority to do business in the State of Pennsylvania filed by Mangaslag, Inc. When completed the plant would consume more than 400 tons of anthracite daily. Source of material for the plant would be approximately 1.2 million tons of steel mill slag produced annually by East Coast plants.

TITANIUM

Potentialities of titanium and its alloys are steadily being realized. With the exception of atomic energy, there is perhaps no other industry engaged in the volume of simultaneous research, development, and production that is carried out by producers, government, users, and potential users. The word *titanium* has become as common as *steel*, although the quantities of each produced cannot be compared on any basis.

That any additional information on the production or uses of titanium is eagerly awaited was evidenced by the attendance at the Titanium Symposium held at the Institute of Metals Div. Fall Meeting in Philadelphia in October 1952. While originally presented as an off-the-record session, JOURNAL OF METALS has obtained the release of most of the papers presented, and these papers follow in this issue.

Those who attended the Symposium were fortunate in being able to hear M. A. Hunter recount his early experiences in producing pure titanium. We have reproduced his paper faithfully, not only for its historical significance, but in an attempt to retain some insight into a man who has contributed much to the profession of metallurgy and metallurgical engineering.

Significantly included are the aims and accomplishments of the Air Force, Army, and Navy, and current work being done by titanium producers and users.

We wish to thank all who contributed to this issue, for helping to spread the technical information throughout industry.

Editor, JOURNAL OF METALS

Early History of Titanium

by M. A. Hunter

THE progress of research in any field of endeavor is not that of a slowly rising tide. But like the breakers on the ocean floor surges of activity are followed by periods of comparative inactivity with the general level of knowledge rising to a higher level between each wave. There can be no better example of this process than in the field of metallic titanium.

The element was isolated in the year 1790 and named after the Titans of mythology in 1795. As the years went on ripples of interest appeared in the literature but more than a century was to pass before the metal was isolated in massive form and another half century elapsed before the full realization of the original discovery was achieved. The frequency of the surges was low but the amplitude was higher in each of the surges and when the overglamourization after each of the surges disappeared, knowledge in the field of interest of titanium was at a higher level than before.

The assignment given to me on this occasion is to describe that intermediate period in the first decade of the twentieth century when massive titanium was first isolated. There are three points in the activity of that period on which I would like to dwell:

M. A. HUNTER has recently retired as Dean of Faculty and Head of the Metallurgy Dept. of Rensselaer Polytechnic Institute, Troy, N. Y., to continue his research at Rensselaer.

1—What caused the sudden rise of interest in the subject of titanium?

2—What was done at that time to increase our knowledge of the problem?

3—What reasons can be assigned for the lapse of interest in the succeeding half century?

My qualifications for the job are merely that I was, by an accident of circumstances, one of the instruments in the development. I arrived in Boston in October 1905—as an impecunious immigrant—in transit to the Paradise in the South Pacific which was my original home. I picked up a job with the General Electric Co. in Schenectady under Dr. Whitney and began operations there on the first of January 1906.

The world at that time was lit by carbon filament lamps of which the best was the GE metallized filament or the GEM lamp. There was feverish activity directed towards replacing the carbon filament with a filament of a high melting metal. VonPirani in Germany had produced metallic tantalum in wire form and we in the GE Laboratory had duplicated his results. But the other metals with high melting points—tungsten, molybdenum, titanium, etc. had not been so produced. Tungsten and molybdenum of high purity were available but all attempts at melting and drawing them to wire had failed. At this particular time, Dr. Coolidge was mixing tungsten or molybdenum powders with cadmium amalgam, squirting the mixture into filament form and driving off the mercury and cadmium by sintering the individual filaments in hydrogen under an inverted dome. The present sintering methods for wire production had still to be born.

But in the case of titanium no pure metal had up to that time been produced. An added interest was given to the problem by the fact that the melting point of titanium was reputed to be of the order of 6000°C, far in excess of the known melting points of the other metals which were then under consideration. Looking at this last statement in retrospect I can only believe that someone was guilty of wishful thinking.

My original laboratory journal of daily operations is not at this time available. That had to be left with GE when my connection there was dropped in July 1908. But copies of monthly and quarterly reports are available which contain the substance of these operations.

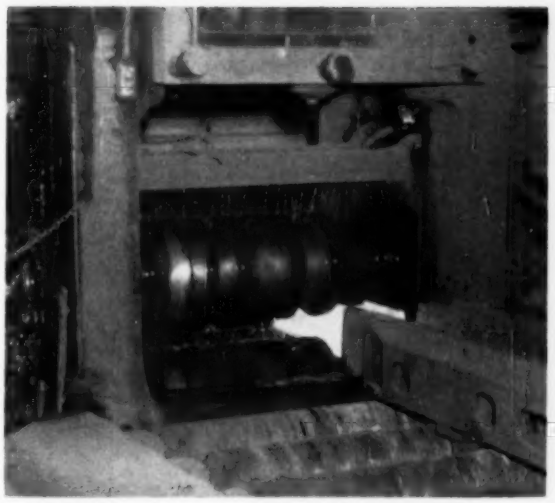
Experimental Observations

In the period between January and April 1906, tantalum and alloys of tantalum with tungsten, thorium, columbium, and zirconium were under consideration. A report of May 1 concludes with the remark, "such was the state of the experiments on alloy mixtures when work was begun of titanium."

A report of July 5 gives the results of attempts to reduce titanium oxide with carbon, "the best results being obtained by reduction in a tungsten crucible at 9 kw where the percentage of carbon sunk as low as 4.6 pct. But it seems doubtful if we can prepare metallic titanium by this method. All experiments up to this point have succeeded in giving us only the bluish purple suboxide TiO mixed with varying amounts of titanium carbide. But though the production of metallic titanium as such would seem to be impossible, we are yet left with one means of producing a filament from the products thus obtained. It is possible to produce a mixture containing 50 pct TiC and 50 pct TiO. If we can bring about a reaction between these substances, then according to the equation

$$TiC + TiO \rightarrow 2Ti + CO$$

we would have a substance available for filament material." A reference to the work of Moissan in producing titanium with 2 pct carbon accompanies this citation. But work on squirted filaments of this character gave unsatisfactory results.



A long way from the first laboratory preparation of pure titanium is this half-ton Ti-150A high strength titanium alloy ingot being bloomed to forging bar size at Watervliet, N. Y., for Titanium Metals Corp. of America.

In the report of September 11 the indigo nitride had been prepared from the complex ammonical compound $TiCl_4 6NH_3$ and the yellow nitride Ti_3N_2 by heating the former in vacuum. The complex titanofluorides had been reduced by the alkali metals potassium or sodium with yields in all cases of products containing less than 80 pct of titanium. The products from these experiments were turned over for the production of filament materials. The report ends with the statement that, "A third method of preparing metallic titanium is now under consideration, viz., the reduction of the tetrachloride at a temperature of 200°C by metallic sodium."

Reductions with Sodium

The first reference to sodium reductions of the tetrachloride appear in a quarterly report of October 27 when titanium chloride was distilled in a boiler-condenser arrangement over molten sodium at low temperatures in a vacuum. A later report of November 20 describes the first successful experiment.

In the hope that this may have some historical interest for you I reproduce the exact wording of the original report.

"An attempt has been made to reduce titanium chloride with an alkali metal. In a previous report it has been already mentioned that the vapor of titanium tetrachloride was passed over molten sodium, but owing to the formation of a protective coating around the sodium no success had been obtained."

"The experiment was then varied. The reacting materials, $TiCl_4$ and sodium, were placed in a specially constructed bomb, with a tightly fitting lid, screwed down well to prevent any possibility of

leakage of the vapor. Some $TiCl_4$, however, escaped, and it is presumed that finally, when the reaction took place, the bomb contained an excess of sodium. When the bomb was opened small globules of molten material were found interspersed through the mixture of a black powder and here and there particles of undestroyed sodium. The NaCl resulting from the reaction had fused completely together. The metallic globules being of most interest, were first analyzed.

"A preliminary examination by dissolving a small portion of the metal in warm, dilute HCl, showed only a small trace of iron.

"Two small beads were then taken and boiled in warm dilute HCl for 3 hr. At the end of that time 0.0611 g had dissolved. The solution was oxidized with HNO_3 and the titanium precipitated with ammonia. The precipitate on ignition weighed

0.1068 g TiO_2

Percentage titanium 104.9.

"The discrepancy is not due to iron, for the presence of that metal would lower the apparent percentage of titanium. It would appear from this rough analysis that the molten globules contained no sodium, as there is no room left in the analysis for it. We have, then, for the first time, melted beads of very nearly pure titanium, the only impurity being a small trace of metallic iron."

A subsequent report—November 1906 to April 1907 describes the enlargement of these operations. The first bomb had 100 cc capacity and accommodated 50 g of titanium chloride and 25 g of sodium, the second had ten times this capacity—500 g of the chloride and 245 g of sodium with a theoretical yield of 120 g of metal. In actual practice from 470 g of the chloride, 107 g of metal were obtained with an actual yield of 90 pct of which 71 g was in the form of slugs or rondelles with 3½ g of medium material and 4½ g in fines.

Two other types of bombs were subsequently made by the Titanium Alloy Mfg. Co. of Niagara Falls. The larger bomb was reputed to have produced 5-lb batches of metal.

Two abstracts from the April report I have just mentioned might be of interest. The first refers to oxygen content.

"The loss of material amounting to 10 pct is accounted for by the fact that some of the titanium is oxidized during the reaction from the presence of oxygen in the sodium used. This oxygen could not be avoided even when the sodium was carefully peeled before introduction into the reaction bomb."

The second reference has some economic interest.

"This method then is an admirable one for producing titanium in moderately large quantities in a fused condition. The cost of the titanium, taking into consideration the cost of the materials only amounts to $2 per lb. The method of preparation, however, is a tedious one. I have therefore sought in experiments to be later detailed to produce the metal by easier means."

These *easier means* involved the réduction of potassium titanofluoride by pyrometallurgical and electrometallurgical methods, the reduction of titanium dioxide with aluminum or with magnesium, the electrolysis of calcium chloride containing titanium dioxide and the dissociation of the "supposed titanium hydrides." Carbon filaments were treated in an atmosphere of titanium chloride and titanium filaments were treated in carbon monoxide from which filaments of titanium oxycarbide were made. But all these are of little interest here.

Properties of Titanium Produced

An analysis of the product gave 99.9 pct titanium. Professor Mixter of Yale to whom some of the material was sent for a determination of the heat of combustion reported 100.1 pct. No sodium or iron could be detected. (Spectroscopic analysis at that time was undeveloped).

In fact it is difficult to see how the product could have had any metallic impurities. If any were introduced they must have come from the commercial metallic sodium and not from the purified titanium chloride which was used. We knew nothing of course at that time about the effect of oxygen or nitrogen on the quality of the product. But again, in retrospect, it is difficult to see how the metal could have taken up either of these since the bomb in all cases was filled practically to the lip. In spite of all this the slugs obtained were malleable when hot, but brittle when cold. My own observations were that small rondelles could be flattened cold and Mixter reported that in grinding up material for his combustion experiments it was impossible to grind to a fine powder—some particles were flattened and others rounded in an attempt to do so. But the brittleness in large pieces has still to be explained.

Forging offered no difficulties if carried on at a low red heat usually on 12 g slugs direct from the bomb. But drawing the material to wire offered some difficulty. "Homogeneous wire of more than 12 in. in length has not yet been obtained nor one of a lesser diameter than 100 mil."

I know I have your sympathy when I reported that "I found a difficulty in melting the metal." No crucibles and no atmospheres would give a satisfactory melt. "A pressed rod of titanium was melted in a mercury arc but the bead on cooling was porous, brittle and had lost all malleability." You have to remember that argon and helium were at that time curiosities in Ramsay's laboratory in London.

Melting Point

Some of the larger frozen chunks of metal were forged below a red heat in air and the melting point determined by passing current through the rod in vacuum. My observations gave the melting point as being between 1800° and 1850°C. On unforged slugs Dr. G. K. Burgess of the Bureau of Standards reported the melting point to be 1795°C ± 15°. By this one act the glamour attached to titanium metal as a filament material disappeared to the great disappointment of myself and G.H.Q. of the General Electric Co. My interests in titanium thereafter were concerned with the use of titanium as a minor constituent in other alloy systems.

In the enthusiasm of my early youth I concluded my original paper in 1910 with the remark:

"A method is here given by means of which moderately large quantities of pure titanium may be produced with ease, so that the mystery which has so long enshrouded this refractory element will soon be dispelled."

Four decades passed before this prophecy came to its full realization. To bring it to pass required the newer methods of melting under argon or helium, the unlimited financial resources of the Federal Government and what is more important the experimental genius of a succeeding generation.

Titanium Is Vital to the Air Force

The Air Force recognizes the important role that titanium is expected to play in the development of superior military equipment, and supports sound programs to help expedite the utilization of the metal and its alloys. Basic responsibilities and problems found in both industry and government are:

- **Support for the basic industry expansion**
- **Responsibility for production improvement, quality improvement, and price reduction**
- **Responsibility for the utilization and application of the material**
- **Responsibility of the military in establishment of a titanium industry**

by Col. John N. Dick

THE titanium industry is expected to make a significant contribution to the national security. This is particularly true in regard to the programs of the Air Force. Industry has been informed of the objectives and desires for this metal and is believed fully appreciative of its responsibility to the aircraft programs.

The achievements to date in building a successful titanium industry are gratifying, but as yet the metal cannot be considered a full-fledged member of the combat team. Industry is to be commended for the excellent progress it has made in the past few years in introducing this metal into military materiel. However, the progress while significant has not been sufficient to date in terms of military urgency. Titanium is so important to the Air Force that a normal 10 to 20-year development program must be compressed into a much shorter period. Headaches, problems and frustrations are inherent in any such attempt to accelerate development to the extent that is now being asked of this metal. It is needed in airplanes flying in Korea today, and it is absolutely essential if military interceptors of the future are to protect our major cities from high speed bombing attacks. It is recognized that the greatest deterrent to a full scale *shooting war* is a modern military machine capable of dealing destruction on the enemy, and capable of defending the United States against an aggressor. Titanium is committed to an important part in accomplishing this objective. It is believed that the nation that adapts titanium successfully to its military equipment will achieve an important advantage over its foes. This advantage must be obtained for the United States.

Progress in aircraft development beyond 1956 is believed dependent to a considerable extent on the availability of proper raw materials. There is every indication that many metals and materials of today,

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because of their inherent limiting characteristics, will be inadequate for the supersonic aircraft of tomorrow. Fortunately, titanium has appeared, and if given the proper support, it should aid materially in meeting new qualitative requirements. By utilizing titanium, it will be possible to design and produce aircraft to operate at speeds which involve skin temperatures in excess of those that can be tolerated by today's conventional materials. Its lower density will permit production of planes of greater maneuverability, longer range and striking power, at higher speeds, in addition to shorter take-off distances than is presently possible with current designs. By the greater use of titanium the Air Force will furnish the necessary stimulation to industry to bring about a lower price. Increased production should improve the quality of the product and sustain the interest of the producers. The Army and Navy also have a vital interest in this metal and are expected to become large consumers at some future date. Likewise, future benefits to the civilian economy are worthy of note.

It would be well to review at this point the basic responsibilities and some of the problems which are currently faced in both industry and government. There are four basic areas to be considered.

1—Support for the basic industry expansion: This is a function of the *Defense Materials Procurement Agency*. This agency has recognized the urgency element involved and has supported those companies prepared to proceed in an expansion program. Current programs now in effect by the sponsorship of this agency represent a possible expenditure of $150 million. Defense Materials Procurement Agency is enthusiastic in expanding titanium production but it must be guided by the military's qualitative and quantitative requirements. Contracts entered into to date are with Titanium Metals Corp. and E. I. DuPont Co. These are for 10 tons each production per day. It is anticipated that further expansion contracts will be awarded shortly. Of those in the fore of interest are Crane Co., Monsanto Chemical, Kennecott Copper, Union Carbide, and several others.

2—Responsibility for production improvement, quality improvement and price reduction: This responsibility belongs to the *Basic and Fabricating Titanium Industry*. The challenge faced by this segment in regard to titanium is similar to that faced by the aluminum industry some 35 to 40 years ago. Production of sponge has grown to a current 4 tons per day and is expected to increase to 20 tons per day by 1954. Many companies, other than those now in production, have evidenced interest in entering into the titanium field. Thus basic production is beginning to show substantial progress. Industry which is now in the process of acquiring the production know-how to form and shape the material for its proper application, has shown great imagination in developing the necessary techniques. However, many problems must still be overcome before a consistent quality of high strength titanium alloys can be furnished in quantity. Although it is known that ultimately the largest demand for titanium will be for alloys, there are sufficient potential users for the unalloyed titanium to consume current production. It is believed that the development of the needed alloys is not far off. Probably the greatest problem facing the industry at present is that of producing consistently high *quality* material in the *quantities* required and on a regular schedule. There is confidence that industry will solve this problem in the near future. Perhaps the time has come whereby, *under government sponsorship*, there can be an exchange of technical alloying information through cooperative effort by the titanium industry, to hasten the day when aircraft quality material will be made available.

3—Responsibility of the titanium *consumer* for the utilization and application of the material: Insofar as the Air Force is concerned, the effective utilization of titanium rests largely with aircraft and engine manufacturers since much of the design and production development is accomplished by industry in their efforts to improve aircraft quality and performance. What specifically are the current problems affecting the increased use of this material by Air Force contractors? One large aircraft company has reported a reluctance to expand its use of titanium, because of its inability to obtain sufficient quantities of consistent quality materials on a regular schedule. To varying degrees this is true of many other aircraft and engine producers. Problems in machining and forming are not unlike stainless steel and to a substantial degree the industry's apprehension in this area has been reduced. It is essential that the aircraft and engine companies incorporate titanium into current models in order that the material may be consumed and therefore make possible further expansion. This is necessary if the U. S. is to remain in the forefront in aircraft development. Engineers and aircraft industry officials concerned with this development must not be discouraged in their efforts, whether the difficulty lies in the temporary inability to obtain the desired type and quantity of material, or, whether it is a problem of design or production.

4—Responsibility of the *military* in the establishment of a titanium industry: The military responsibility centers principally in the fields of research, development, and procurement. Considerable work in supporting the titanium industry has been accomplished by the military departments. There is every indication that the Army is prepared to move forward without delay in using titanium as soon as the price has been substantially reduced and the necessary quantity of material is available. The Army is to be commended for the orderly manner in which it has approached its research and development problems. The Navy also has an active program in view of the excellent noncorrosive qualities of titanium as well as a common interest with the Air Force in the use of the material for aircraft. The Air Force depends largely on its contractors for carrying forward a large share of its development program. This is not to imply that Air Force research and development people are not active. They are in fact doing both basic and applied research and development, through industry and qualified institutions. Some major programs are in welding, brazing, heat treatment, creep, determination of diffusion rates, as well as development of titanium alloys. Production development work includes applications in spacers, rings, blading and other compressor parts in jet engines. It includes firewalls, nacelles, fuselage structure, shrouding and other stress bearing members in the airframe. Because of the weight advantage offered by titanium literally every aircraft part has been considered for design in titanium. Secretary of Defense Lovett recently announced that, "when 1 lb of weight is added to a plane 10 lb must be added to the structure at a cost of about $400." When one considers the relation-

ship of this statement in the reverse it is easy to see how titanium becomes economical for use in aircraft.

It is essential that the four elements—the Defense Materials Procurement Agency, the basic and fabricating titanium industry, the titanium consumer, and the military—work in harmony if maximum success is to be achieved in the shortest time.

The Air Force policy has been and will continue to be:

1—Advise other government agencies, including the Defense Materials Procurement Agency of Air Force interest in this metal.

2—Encourage the industry in its efforts to expand production and improve the quality of its material.

3—Aggressively continue such basic and applied research as is necessary in furtherance of the program including the development of production know-how with aircraft and engine manufacturers.

4—Support Air Force contractors in their efforts to use titanium by allowing for a fair share of the increased costs encountered.

In support of these objectives it was announced to contractors that the Air Force is willing to accept its fair share of the increased costs incurred through the use of titanium. By paying premium prices even for marginal uses some advantages are obtained, but not nearly as much as will ultimately be gained through design and engineering. By such pump priming, a decline in price can be expected. This is the basic policy of the Air Force and is the motivating factor behind all actions.

The Air Force has recently authorized Convair to incorporate titanium in production quantities in the B-36 airplane. Similar authority will be granted in the future to other Air Force contractors, to use titanium in existing production items. This will permit contractors to develop the necessary manufacturing skill and know-how which will be reflected in the design of future models. Titanium is needed in engines, airframes, and pilotless aircraft or guided missiles. It is needed not only in complex areas and major components but also in such simple forms as bolts and nuts. Wherever it is possible to save weight and translate the saving into greater range or increased pay loads—titanium is needed. To satisfy these needs titanium will be required in forgings, sheet, bar stock and in all sizes and shapes. It must have the properties of strength and heat resistance with good structural characteristics; however, in some applications, it need act only as a separating wall. The point is—it must be versatile and adaptable to many applications.

The Air Force recently has established at the Air Materiel Command, a committee, designed to insure the maximum use of titanium. This committee will coordinate Air Force activities in this field and will recommend needed actions to insure the rapid and efficient application of titanium in aircraft production programs. In addition, this committee is to be the focal point for the collection and dissemination of technical information to contractors. This committee formalized the policy of Air Force Headquarters, and recognized the need for an immediate application of titanium in current aircraft production. The Director of the Production Resources Div. under whom this committee was formed has summarized the position of the committee thusly: "Industry can expect to be requested for some serious thinking, relative to the efficient production and use of titanium. Development in the art of producing and fabricating this material may well be financed by the government, but must of necessity, be in the main accomplished by industry."

In addition, the Munitions Board recently has recognized the need for a high level policy committee in the Dept. of Defense to expedite the development and use of titanium. This committee currently is being established with members of general and admiral officer rank. Gen. Troup Miller of Headquarters USAF will be the Air Force member. The committee will be responsible for the formulation of Dept. of Defense policy relative to procurement, development, financing and the use of titanium in military equipment. This will allow the budgeting, procuring, and production organizations of all three military departments to move more freely and rapidly into the adoption of titanium as a standard production material.

It is believed a similar committee should be established at the level of the Office of Defense Mobilization. This would permit discussion and formulation of policy decisions at the highest levels of government. Such a committee already has been informally discussed—and it is hoped some constructive action will occur in the near future. It should be the organization expected to coordinate the four basic elements which have been previously mentioned. It is only closely integrated and coordinated action that can speed up the metals growth. Defense Materials Procurement Agency, the producing industry, the consumer, and the military must walk arm in arm down the same road if the penalties of ignorance of each others actions are to be avoided. Some have thought of this body or committee in terms of a czar; think of it in terms of an agency to bring about cooperation and thereby avoid costly mistakes and delays.

While much effort remains to be made to bridge the gap between the production and consumption of titanium, the Air Force is satisfied that remarkable progress is being made. It is only a matter of time until titanium will be in full demand for the production of military equipment. While the problem seems to be predominately one of using the available titanium today, the major emphasis must soon be shifted to that of further increasing the basic production of titanium and its alloys. The Air Force wants titanium and its alloys in its aircraft as soon as possible. It actively endorses and supports any sound program which aids in achieving this objective.

The military are often forced by circumstances to support enlargement of industries which have no value to the peacetime economy. These actions do not represent waste so far as National objectives are concerned, but are often necessary to this country's very survival. There is, in titanium, a potential new industry that takes off at the point where the military leave off. It is not a *war baby*. Titanium is a metal that will play a significant role in the national economy. Titanium is a metal that will take its proper place in the family of materials, and in so doing, will contribute to the betterment of mankind. Titanium is a metal that requires the conscious effort of all; government, industry, military, scientist and engineer, and citizen if the immediate objective is to be achieved. The objective is a more efficient and hard hitting military machine, and by this accomplishment, it is hoped, peace in our time.

Titanium Evaluated for Ordnance

by Col. Benjamin S. Mesick

TITANIUM was isolated in a crude metallic form as early as 1825, but remained essentially undeveloped until about 1940 when the necessary technological advancements became available for semi-commercial production.

In 1948 the Bureau of Mines and several laboratories in the country were producing a few pounds of commercially-pure titanium for experimental purposes. By the fall of 1950 total titanium production had risen to an annual rate of some 60 tons. In 1951 industry production rose to 700 tons and an output of at least 5000 tons is anticipated for 1952.

Titanium is found in nature chiefly as rutile (TiO_2) and ilmenite ($FeTiO_3$), both plentiful in the United States. In fact, titanium is the fourth most plentiful structural element in the earth's crust, surpassed only by iron, aluminum, and magnesium. The ore is refined in two steps: 1—Separation of relatively pure rutile either by smelting or by standard ore beneficiation methods, depending on the nature of the ore, and 2—reduction of the oxide to pure titanium. In the reduction process as used today, the titanium is extracted from the oxides by halogenizing to secure titanium tetraiodide or chloride. One of these compounds is reduced to metallic sponge by either the iodide or the Kroll processes. Although the iodide process yields the purer metal, the Kroll process or one of the modifications of this process is the method responsible for the greatest tonnages of metallic titanium.

Titanium possesses an unusual combination of intrinsic properties. It is a silvery-gray, light, corrosion resistant, tough, strong, paramagnetic metal. Its weight, (0.16 lb per cu in.) is 40 pct less than steel (0.28 lb per cu in.) and only 60 pct more than aluminum (0.10 lb per cu in.). It combines the corrosion resistance of stainless steel with the lightness of the strong aluminum alloys and possesses certain definite advantages over both. One outstanding advantage is its high strength which is comparable to that of heat-treated steels, while its density is only slightly over half of these materials. It is highly corrosion resistant, being greatly superior to aluminum, better than many specialty steels, and unique among the common engineering metals in its complete immunity to salt water and marine atmosphere. In structural form pure titanium tends to creep under constant load. This characteristic however is practically eliminated by cold work or alloying. Under some conditions titanium is difficult to fabricate and without some form of surface conditioning tends to gall and seize in applications involving moving contact. It has been found practically impossible to weld titanium to many dissimilar metals but it is to be expected that many of the present difficulties will be overcome in the not too distant future.

The maximum advantage from the use of titanium can only be obtained from substitution of alloys equal in strength to the steel alloys presently used. In making such substitutions consideration must be given to the characteristic differences in mechanical properties between steel and titanium. One important consideration is the modulus of elasticity, which for titanium is only slightly more than one half that of steel. This low modulus permits much greater deflection for the same load, and can result in structural instability and possibility of fatigue troubles with component fastenings, studs, bolts, etc. In many cases complete redesign is necessary to achieve maximum weight savings and still retain rigidity and functioning characteristics. Recently there appear possibilities of bettering the modulus by alloying.

Another important but little considered factor is the characteristic tensile stress-strain curve for titanium, which is very similar to that of aluminum; a gradual curving or yielding at relatively low values. Thus, in making substitutions on a strength basis it is essential that the yield strengths be comparable at the proportional limit; approximately 0.01 pct offset, and not at the 0.20 pct offset value generally reported for titanium and titanium alloys. In Ordnance applications these factors are of extreme importance in view of the low factors of safety and performance characteristics involved. Contrary to many industrial applications. Ordnance equipment must operate satisfactorily at temperatures from $-25^\circ F$ to $+125^\circ F$ and over long periods of time. Components, particularly those which may be subject to air transportation or hand carried by troops, must be as lightweight as possible, yet possess the strength and rigidity necessary for the service required.

Commercially pure titanium and titanium-base alloys are available in the form of sheet, strip, plate, wire, bar, rod, forging billets, and forgings. Welded and drawn tubing up to 3 in. OD is also obtainable. Hot extruded and cold drawn seamless tubing and hot extruded bar-size shapes will probably be available within a short time. Castings, other than in

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ingot form, are not available commercially because of difficulties from refractory and gas contaminations. However, extensive research is being conducted, and it can be assumed that within the next year a sizeable number of castings will be produced by special techniques.

The physical properties obtainable from titanium and titanium-base alloys range roughly from 40,000 to 200,000 psi yield strength; 50,000 to slightly over 200,000 psi tensile strength; and elongations from 30 pct to 2 pct. The impact properties, in general, scatter to a disconcerting degree, probably as the result of variables in mill processing. Trace elements also may influence the impact values. With improvements in alloying and processing, the impact properties have markedly increased and further improvement should be expected.

In the fabrication of titanium and titanium-base alloys the principal difficulty has been in the machining of welded components where cutting into or through weld metal is involved. Specific cases are pads built up with titanium weld deposits, and oversize fillets, or excess of weld metal in areas which must be removed during machining operations. Investigation has shown this condition to be caused by oxidation of the surface of the weld deposit resulting from lack of complete shielding during the welding operation. At temperatures of approximately 1600°F and above, titanium rapidly absorbs nitrogen, oxygen, and hydrogen, and unless completely protected from atmospheric contamination by inert gases a hard oxidized surface layer will be obtained.

There appears to be three possible solutions to this problem:

1—Design so that no weld deposited metal projects into areas which are to be machined.

2—Complete shielding by an inert gas throughout the entire welding operation and maintained until the metal has cooled to a temperature below 1200°F.

3—Use of an electrode coating which will form a deposit on the surface of the metal to prevent oxidation from atmospheric contamination.

Of these possible solutions engineering design offers the only immediate hope for eliminating such machining difficulties. Complete inert gas shielding is practically impossible to accomplish in general production welding, and no suitable electrode coating has as yet been developed which will adequately prevent surface contamination.

In general, it has been the experience of the Ordnance Corps that fabrication of titanium and titanium-base alloys by methods involving forming, forging, machining, and grinding, can be accomplished without much difficulty, and in most cases about as readily as with alloy steel. The most important consideration is in the initial selection of the type of alloy best suited for the purpose. Several items have already been fabricated from titanium and others are under review and consideration.

One of the items recently fabricated, tested, and authorized for production is the 81 m/m Mortar Base Plate. This was formerly made as a welded steel structure in two sections and weighing a total of 48 lb. Two men were required for transporting this assembly. Because of its lightness and strength, titanium allowed redesign to a one-piece welded construction, weighing only 24 lb; this releases one man for other duties.

Other items for which titanium is being substituted, and which are currently under test are armor plate for tanks and vehicles, and flash suppressors. Present indications are that titanium-base alloys can be produced which will be satisfactory for these purposes, and which will result in a considerable saving in weight and improved maneuverability of the equipment. Structural components such as outriggers also were fabricated and are being tested.

Tests have also been made to determine the possible application of titanium for helical springs. Such springs formed from commercially rolled or drawn material exhibit low fatigue life as the result of surface oxidation produced in the manufacturing operations. It is expected that the use of centerless-ground stock may overcome this condition, and insure a satisfactory product.

In addition to the items mentioned, a program has been initiated to review all types of standard Army equipment pertaining to the individual soldier with a view toward using titanium wherever it will lighten the load or reduce physical effort. In all cases where the resulting lightened item is at least equal in properties and performance to present equipment serious consideration will be given to the adoption of the titanium version as standard.

On the negative side, titanium is not generally suited for applications involving sustained temperatures much above 1000°F. There are indications that alloys may be devised which will so modify the characteristic high temperature reactivity as to permit worthwhile service life up to possibly 1500°F. While titanium can be surface hardened by nitriding or carburizing, the temperatures required for these operations are such that the physical properties may be adversely affected. This effect is being investigated extensively because of its importance.

Research investigations have indicated that coatings of titanium-silicide offer protection up to 2000°F, and such coated products may show satisfactory performance where exposure to hot gases is involved. Investigations have also shown that anodic coatings produced on titanium by chemical or electrochemical methods can be effective in reducing wear and galling. No method of plating has yet been devised which will provide adequate adhesion of nickel or chromium to titanium. However, methods have recently been developed whereby titanium can be copper plated and then joined to other metals by soldering. Intensive research may eventually lead to a solution of the plating problem.

A considerable portion of the output of the common engineering metals is in the form of cast to shape parts, and there are many potential applications for titanium if it could be made available in that form. Because of its high reactivity, however, it is possible to cast titanium in the conventional manner only by melting in a graphite crucible and pouring under vacuum or inert gas into molds made of carbon or other refractory materials. Under these conditions a high carbon metal is produced which possesses low ductility and poor welding characteristics. Several research projects are underway to explore new methods for casting low carbon metal which are sufficiently far along to indicate that excellent castings can be made up to 10 lb or even 20 lb in weight. The casting procedure cannot yet be considered to have reached the commercial stage, but it can be reasonably assumed that within the next year a sizeable number of castings of larger size will be produced.

Navy Has Large Titanium Program

by Edward L. Beardman

DURING World War II and in the hectic days that followed, it became evident that in event of a future emergency this country would be faced with a shortage of various materials. This shortage of materials could severely hamper defense efforts. Thus, it became necessary to redesign equipment so as to conserve these critical materials. It also became imperative for the material engineers and metallurgists to develop new materials. These steps still are necessary to increase chances of success.

Titanium is very inert to sea water and marine atmosphere. It is one of the few known high strength structural materials that have corrosion fatigue in salt water closely approaching that in air. Titanium also exhibits immunity to many chemicals that pit and deteriorate most other metals.

The low density and high strength of titanium will permit reduction in weight for structural applications. This means more supplies can be carried which will permit long cruises for ships and longer flights for aircraft. Its corrosion resistance and corrosion fatigue properties will mean less repairing and thus, less time in the ways for ships and at naval repair stations for aircraft for overhauling. From this it is evident that efficiency will be increased and operating costs reduced. Titanium's resistances to fuming nitric acid exceeds that of stainless steel. This chemical is used in some rockets and guided missiles. The use of titanium or titanium-base alloys in this application may permit the carrying of more fuel or more explosives or a desired combination of the two. Under actual battle conditions the effect of such improvements would be of immeasurable value.

The possibilities for the use of titanium are far reaching. However, the actual production use of titanium and titanium-base alloys in terms of tonnage consumption by the military is still largely a matter of wishful thinking. Speaking for the Navy Dept., it is possible to point to a steadily growing list of titanium applications in naval equipment. But, it is also a fact that its present use could and would be much larger if it was not necessary to contend with costs, budgets, availability, and the like. At this point, it may be desirable to deviate a little to explain the influence of budgets. At the beginning of each fiscal year, Congress appropriates certain funds. The amount of these funds appropriated are for definite programs. Thus, any huge increase in costs for any material reduces the amount of money for other essential programs. To utilize large tonnages of a material as costly as titanium, allowances for its use should be made when the budget for the Navy is being prepared unless the increased costs can be recovered by decrease in construction and manufacturing costs of the various components. From this, it is evident that three major problems in the field of titanium are:

1—High cost

2—The nonavailability of large tonnages

3—The lack of data in applications

When mentioning costs, budgets and availability limiting its use, it was not meant to imply that the Navy has all the answers and is ready in a big way to use more titanium. However, there are a number of straightforward applications for titanium in naval equipment involving no especially involved test programs, or which have already been tested to the extent that they now appear ready for service use. Methods are presently being sought that will permit the exploitation of titanium applications in this category.

On the other hand, there are types of applications that are considerably more involved either because of their critical structural nature or because of fabrication problems that required extensive testing and development programs. Naturally, these are the items that for the most part would be classed as the large consumers of titanium and again cost becomes the major stumbling block. These items include:

1—Submarine snorkel tubes, superstructure and fairwater construction

2—Shipboard condenser and heat exchanger tubes and globe valves

3—Aircraft landing gear components and propeller blades

4—Armor plate.

Nevertheless, it is in this category that the Navy is presently exerting its major development effort.

The current Navy titanium development program is threefold in scope. It embraces: 1—Metallurgical development, 2—study of fabrication techniques, and 3—development and evaluation of specific components fabricated of titanium. In many instances, notably in the development of specific applications for titanium, it has been necessary to combine these three areas of research and development to obtain desired results. The development of titanium alloys for submarine snorkel tubing, superstructures and fairwater construction, alloys for globe valves and condenser and heat exchanger tubes are examples of this type of program. Each of these applications is requiring development of suitable alloys and an extensive study of fabrication techniques to attain acceptable end products. On the other hand, there are numerous programs, although not primarily aimed at an immediate application, being undertaken in anticipation of problems expected to arise in connection with planned applications. Forming of titanium sheet, welding studies, and investigation of the seizing and galling characteristics of titanium are typical examples. Finally there is that type of research which is directed at providing information of a fundamental nature, the benefits of which are reflected in increased knowledge of titanium and its metallurgy and which may result in improved titanium alloys.

The Dept. of the Navy's efforts in the overall titanium program have striven to place the proper emphasis on each of the phases of research previously outlined. The Office of Naval Research is administering and coordinating a very broad and basic program in the metallurgy of titanium.

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The Bureau of Aeronautics, presently is conducting evaluation studies of three promising titanium alloys: Two for sheet applications and one for forging of aircraft components. Some of the present applications for titanium and titanium-base alloys in Naval aircraft are given in Table I.

In addition to these uses for which titanium and titanium-base alloys are being used in naval aircraft, airships and helicopters, the Bureau of Aeronautics is considering the following production uses in aircraft:

1—*Forgings* for landing gear components, compressor blades and disks.

2—*Sheet* for turbine liners, fire shield, fireseal, baffles, stabilizer cover plate, firewall assemblies and inner skin assembly, blast cone splice strip, lower skin, louvre vanes and the corrugations. Other contemplated uses for sheet are in the tail cones, tail pipes and engine shroud.

3—*Bars* for compressor bolts and miscellaneous hardware.

4—Titanium is being considered for vaporizing plates, armor plate, propeller blades, turbine nozzle support, compressor couplings and compressor running rings. It has not been developed as to what titanium mill product will be used for the items.

The Bureau of Ships is particularly interested in the various properties of titanium and titanium-base alloys that enhance its use in designing shipboard machine components and equipment and includes among its programs, methods and techniques of casting titanium shapes. Such shapes as pump wear rings, valve bodies and pipe fittings have been cast successfully. Plans are underway to expand this project to determine the feasibility of converting the techniques to plant scale operation. Fusion welding and resistance welding techniques for titanium and titanium-base alloys are also being studied.

At present, the Bureau of Ships has no current production uses for titanium. Neither has it any contemplated production uses. It must be remembered that the complexities of naval ships and submarines have few equals. Thus, it is essential that the various physical characteristics be tested to determine if any flaws exist. It is then necessary to determine how to either eliminate these flaws or to compensate for them. After it has been determined that the component has a definite shipboard application, it is then tested under actual operating conditions. That is, the item is installed aboard a naval ship for testing under actual operating conditions. From this, the reason for delay in actual or contemplated production uses is readily evident. While the Bureau of Ships at present may not be using titanium in actual or contemplated production, it has a comprehensive program for its use in prototype production. Some of the applications of titanium and titanium-base alloys in prototype production in shipbuilding are:

Bars for turbine blades in low temperature steam turbines.

Castings (permanent mold) for wear rings in salt water pumps; valve body, valve seat and disk in salt water valves.

Plate for meter disk in gasoline meter; wet exhaust muffler in diesel engines, 8-ft section snorkel pipe in submarine snorkel system; and hot water tanks in machinery equipment.

Tubing for salt water valves; condensers; and heat exchangers.

In addition to the aforementioned prototype production uses, the Bureau of Ships is also contemplating the following prototype production uses for titanium and titanium-base alloys.

Bars for control shafts in electronic equipment; antennas in radar; compressor blades in gas turbines; and propeller shafting in minesweeper propulsion equipment.

Castings for microwave cavities in frequency meter; impellers in salt water pumps; fire hose nozzles in firefighting equipment; and deck pressure-proof fittings in submarine electrical equipment.

Plate for wave guides in radar; navigation light shields in navigational equipment; and machinery vents and boxes in deck equipment.

Powder for compressor blades in gas turbines.

Sheet, in addition to the uses for which plate is being considered, could be used in antennas in radar; shock mounts in machinery equipment; and topside machinery label plates in deck equipment.

Tubing for antennas and whip antennas in radar, and mircowave cavities in frequency meter.

Wire for resistance wire in electronic equipment.

The Bureau of Ordnance's program is very small. This is because the Bureau's largest requirement for material is for shells and projectiles. The Bureau of Ordnance is considering testing titanium and titanium-base alloys for the gun, guided missile and armor plate programs.

It is evident that the Navy is alert to the possibilities of titanium and its alloys. The Navy initiated its titanium research program in 1946 and will continue to do its utmost to utilize titanium wherever practicable. The goal is to place titanium in a responsible position functionalwise and costwise.

It must be remembered that it took almost 50 years to develop aluminum and 25 years for stainless steel. Titanium has only been active for five years, and is, therefore, only an infant as a metal. Industry and government have made tremendous progress in exploiting this new material.

It is believed that titanium is certain to make its mark both in war and peace. It is to be remembered that in peacetime, the dollar cost of any material is of great importance to the Navy. However, in wartime the military value of a material usually outweighs the dollar cost.

Table I. Present Applications for Titanium and Titanium-Base Alloys in Naval Aircraft

Form	Uses
	Engine
Forgings	Compressor disks, Cover, Spacers, Blades
Tubing	Compressor rotor disk spacer tube
	Airframe
Sheet	Door installation of main landing gear Center wing structure Center wing front bulkhead Shouds Ammunition boxes, Clips Deck aspirator assembly Channel, Doublers Skin, Angle Flame seal, Formers Hot sections, Firewalls Center and lower fuselage webs Floor and door assemblies in helicopters Various fuselage parts
Strip	Engine access panel assembly case Link door assembly Cabin air valve guard assembly Electronic access door assembly

Titanium Production at Rem-Cru

by Walter L. Finlay, C. E. Newcomb and M. Anthony

DURING the past year results began to replace the speculations that surrounded titanium's debut hardly more than four years ago. Recent Rem-Cru contributions fall into four categories:

Melting—Large titanium ingots are now available—since the 1952 steel strike, Rem-Cru has been averaging 1200-lb ingots in routine production and even these large ingots have now been superseded.

Tonnage-Style Processing—Since resumption of operations after the strike, Rem-Cru has been melting at better than 10 tons of ingots per week and has successfully produced the first wide, thin titanium strip—3 ft wide, 0.015 in. thick, 460 ft long.

Production Uses—After four years of testing, design and prototype evaluation, titanium is now going into production applications. Lockheed and North American jet fighters are using RC-70 and RC-130-A parts and Douglas, in the airframe industry's first nonmilitary application of titanium, is using RC-70 in the nacelles of the DC-7. One jet engine manufacturer is going into tonnage trial production using RC-130-B forgings.

Alloy Development—In the ABC family of all

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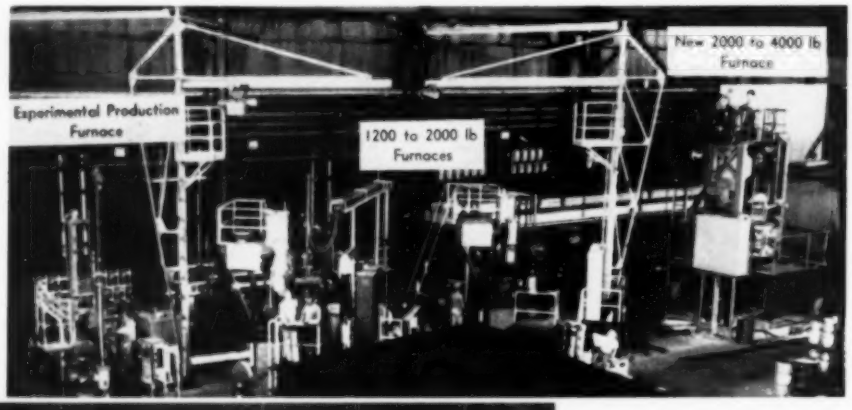

Fig. 1—The Rem-Cru melt shop at Midland, Pa. has doubled in size since this photograph was taken last summer.

Fig. 2—This 2-ton RC-70 ingot, representing $20,000 worth of metal, is the largest titanium ingot ever cast.

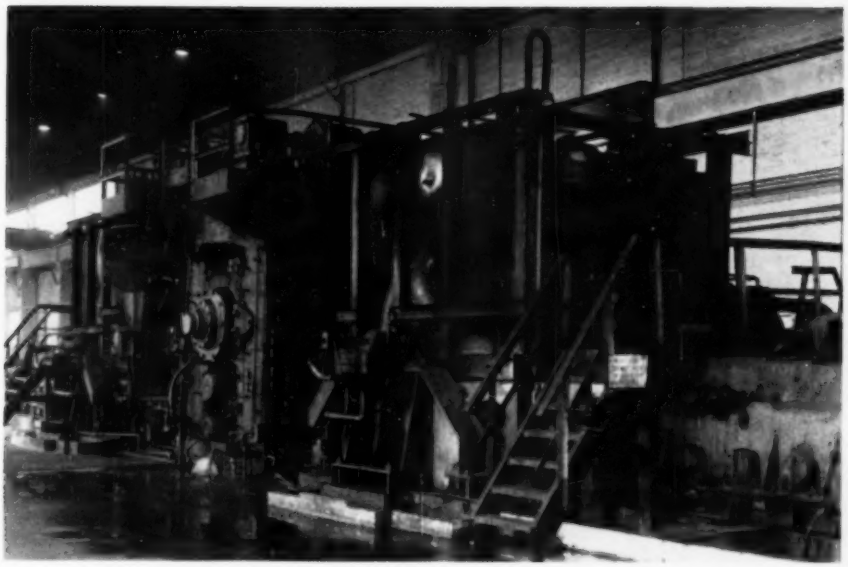

Fig. 3 (left) — This 27x49x66 in. 4 high reversing hot mill and furnaces built by United Engineering & Foundry Co. are an example of the equipment available at Crucible Steel Co. of America.

Fig. 4 (below)—Thin titanium strip, 0.015x 37 in. and 460 ft long was produced of RC-70 using the mill shown in Fig. 3 and the 36 in. Sendzimer mill of Washington Steel Co.

titanium-base alloys, the C (combined alpha-beta) type will shortly be joined by the A (all-alpha) type with greatly improved hot strength and with excellent as-welded ductility.

Each of these is a major milestone. Together they establish that tonnage titanium winning, melting, alloying, and fabricating arrived during 1952.

Fig. 1 shows the Rem-Cru melt shop in Midland, Pa. This photograph was taken last summer. Since then it has been doubled in size. In the left foreground are a number of 1200-lb ingots, produced in the cold mold furnaces shown in the rear center. They were the titanium giants of 1951. But in the fast-moving titanium industry, yesterday's giants are today's pygmies. The furnace on the far right is now producing ingots which actually dwarf the 1200-lb ingots. It has produced the largest titanium ingot ever cast—the two-ton RC-70 ingot shown in Fig. 2. This was accomplished 2½ months ahead of schedule, and contains $20,000 worth of metal.

Such large ingots as 1200 to 4000-lb merit tonnage-style processing for at least two important reasons. First is lower processing cost per pound. Second is quality—considerably less time is spent at contaminating elevated temperatures; moreover, the entire ingot is treated more uniformly. Fig. 3 shows an example of the modern mill equipment available to Rem-Cru from one of its parent companies, Crucible Steel Co. of America. The illustration shows the Midland four-high hot reversing mill with automatic coilers which are contained in the furnaces shown just before and after the roll stand.

Using this and associated continuous strip equipment, Rem-Cru has pioneered wide, thin strip. Below 0.020 to 0.025 in., the 36 in. wide Sendzimer mill of the Washington Steel Co. is employed. Fig. 4 shows the first successful wide, thin titanium strip produced anywhere. It is RC-70, was produced last summer, and is 0.015x37 in. x 460 ft.

As indicated, this ultimately means lower cost and higher quality. Existing quality, while leaving room for improvement by better processing, nevertheless is good. Distribution curves were obtained recently for individual tensile data in regular quality control work on RC-70. Thicknesses range from 0.015 to ⅛ in. Over 50,000 lb of ingots are involved. All are from a particular period and no RC-70 ingot during this period was omitted. Yet the distributions are normal and the ranges are not excessively wide. For example, 95 pct of all the yield strengths fall within a 20,000 psi band.

Tonnage-style processing of more than 10 tons of ingots per week both requires and makes possible tonnage production uses. One major tonnage market for titanium is the compressor end of jet engines. RC-130-B is in large trial production on jet engine compressor wheels, blades, housings and associated parts. Air frames are another major market. In addition to several jet fighters, production quantities of titanium sheet are being used on the new Douglas transport, the DC-7. This is shown in Fig. 5.

Fig. 6 illustrates that titanium exists in two allotropic crystal structures: Alpha (hexagonal) and beta (body-centered). It shows moreover that, depending upon the kind and amount of alloying element, one can have either an alpha, beta, or combined alpha-beta structure.

Each of these structures has different properties. Table I gives the overall advantages and disadvantages of each.

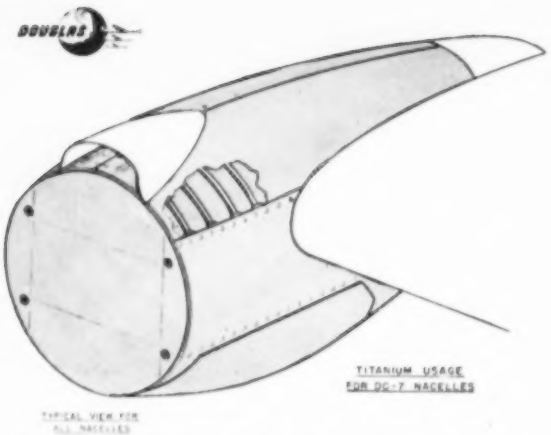

Fig. 5—Titanium usage for Douglas DC-7 nacelles is shown in this typical view for all nacelles.

To date, all commercial titanium-base alloys have been of the combined alpha-beta type. These will shortly be joined by a new Rem-Cru alloy of the all-alpha type. Two compositions are currently being evaluated. Whichever is selected will almost certainly contain aluminum. The annealed, binary Ti-Al data of Fig. 7 are therefore pertinent. These data were obtained by Battelle under Rem-Cru sponsorship.

Table I. Properties Related to Titanium Structures

Structure	Properties
Alpha	Best all-round performance Good weldability Good strength hot and cold Good oxidation resistance Fair bendability
Beta	Best bendability Excellent bend ductility Good strength hot and cold Vulnerable to contamination Large consumer of strategic alloys
Alpha-Beta	Best for combined performance Good cold strength Good bendability Moderate contamination resistance Excellent forgeability

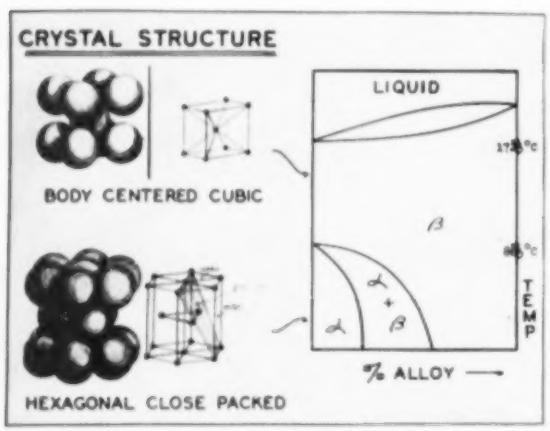

Fig. 6—Titanium exists in two allotropic crystal structures, and depending upon the alloying additions, one can have an alpha, beta, or combined alpha-beta structure. Each structure has different physical properties.

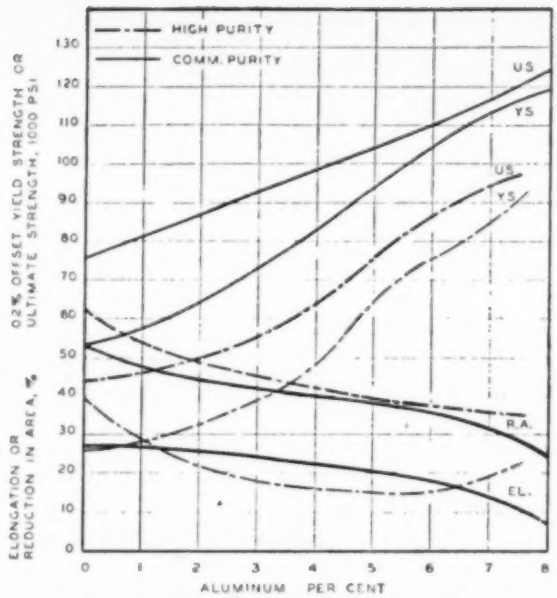

Fig. 7—Data for annealed, binary Ti-Al alloys are important because a new all-alpha titanium alloy will almost certainly contain aluminum.

The good hot strength and weldability of the prospective new all-alpha alloy promise to meet a number of important requirements hitherto out of reach of any titanium product.

Rem-Cru's supplier, the DuPont pigments dept., is making ample quantities of good quality sponge; melting capacity is larger than the supplier's sponge capacity; titanium is beginning to be processed in tonnage style; several production uses have been established; and new and improved alloy types are on their way.

This is the overall picture and it is surprisingly good considering the infancy of the titanium industry. Two elements in the immediate picture merit discussion to show their consistency with this overall situation. These are: 1—The existence of a Government stockpile of approximately 250 tons of titanium sponge and Rem-Cru's request to the Defense Dept. for more production orders for bar, sheet, and forgings; and 2—some recent delayed deliveries on standard products RC-70, RC-130-A and RC-130-B.

The apparent inconsistency between delayed deliveries and requests for more orders is reconciled by the fact of last summer's steel mill strike. Rem-Cru has RC-70 sheet, bar, and forgings and RC-130-B bar and forgings in routine production. Delivery delays on these products was occasioned by the 9-week steel strike and its aftermath of production turmoil. Good deliveries on these standard products can now be made and it is on these that more orders are wanted. The titanium in the Government stockpile will do everybody a lot more good if converted into jet engine and plane parts rather than if left in the stockpile.

RC-130-A sheet is in a more developmental stage than RC-70 and RC-130-B. Not only were 9 weeks production lost during last summer's strike but, equally bad, 9 weeks of technical progress were lost. However Rem-Cru is now up to tonnage production of RC-130-A sheet and is making good progress in reducing it to routine production.

Application of Titanium Sheet-Strip Limited by Presently Available Alloys

by J. W. Sweet

THE present status of titanium sheet and strip can be developed best by reviewing the experiences of fabricators attempting to put the material to an end use. The Boeing Airplane Co. as one of these fabricators first became interested in titanium as a possible material for airframe construction in July 1949. At that time experimental quantities had been produced from 70 lb ingots. Some developmental work had been done on alloys but only commercially pure metal was available for testing purposes. It was estimated that production would be about 1 or 2 tons per month in 1950. It was evident that the metal could not be considered for immediate production use. However, it could be considered on a limited experimental basis so that forming and fabricating experience could be gained.

In considering the possible substitution of titanium for currently used material it was decided that at least a 25 pct savings in weight should be realized to make the substitution pay considering the expense and problem involved in introducing a new material into the factory. There had been some indication that alloys of currently used materials were being developed which would result in at least 10 pct higher allowables so this was also considered. On this basis, to substitute titanium for aluminum alloy having 77,000 psi tensile strength, an alloy would have to be developed with an ultimate strength of 175,000 psi. The yield strength should be approximately 90 pct of the ultimate and the elongation 15 pct in 2 in. This was arrived at by calculating for a 25 pct advantage on a strength weight basis plus an additional 10 pct assuming the development of higher strength aluminum alloys.

On the same basis to substitute titanium for steel having 200,000 psi, an alloy would have to be developed with an ultimate tensile strength of 162,000 psi. Of course, there are other considerations that would change these ideal values. In applications involving heat, an alloy having good strength over 250°F could be substituted for aluminum alloy even if its strength was appreciably under the proposed 175,000 psi, as aluminum alloys lose their strength rapidly above 250°F.

Considering the problems involved in developing an alloy it was realized it would be some time before alloys of the strength proposed would be available. In reviewing the properties of commercially pure sheet, it appeared that there was a possibility of substituting it gage for gage in replacement of annealed stainless steel and realize a weight saving

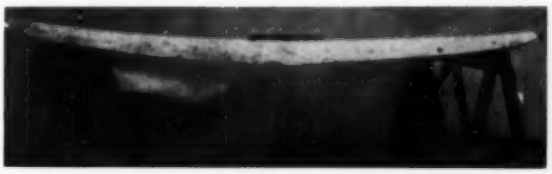

Fig. 1—This length of 0.025 gage commercially pure titanium was stretch formed in the Sheridan stretch press at 450°F.

of 40 pct. This would be for nonstructural and secondary structural applications. Because of availability any consideration would have to be on an experimental airplane. It was decided to consider the use of commercially pure titanium on the XB-52 airplane as an alternate material to stainless steel where a weight saving could be realized. It was further decided to test any available alloys but to confine the possible use for parts to commercially pure material until the alloys were proven. This turned out to be a wise decision considering the availability of sheet alloys to date and their limited properties.

In the initial investigation of the possible uses of commercially pure titanium on the XB-52 airplane it was considered for the engine nacelles, for the replacement of stainless steel sheet in firewalls, and the nacelle cowling. In this use it would be necessary for the titanium to have room temperature properties comparable to 18-8 stainless steel and to be capable of withstanding flame impingement for relatively short periods. Another possible application was for ducting to transfer hot air. In this application it would be necessary for the material to have short time tensile properties at 500°F equivalent to 18-8 stainless steel.

Two sources for commercially pure titanium sheet were available. Because of difference in melting practice the minimum mechanical properties quoted by the two sources differed by 20,000 psi. To cover both sources, two specifications for the material were written and orders placed late in 1949. Three sheets of 0.025 and one sheet of 0.035 gage were received in March 1950 from Allegheny Ludlum Steel Corp. In July 1950, five sheets of 0.050 gage were received from Remington Arms Corp. Specimens from this material were used to determine the room

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Fig. 2—Rear bead upper cowl formed in the drop hammer at 550°F by staging using 0.042 gage commercially pure titanium-condition "A".

temperature mechanical properties and short time tensile properties at 500°F. Allegheny Ludlum Steel Corp. material developed an average ultimate tensile strength of 75,000 psi and a yield strength of 55,000 psi. The Remington Arms material developed an average ultimate tensile strength of 90,000 psi and a yield strength of 70,000 psi. The yield strength of both materials dropped off quite rapidly with temperature, averaging 20,000 psi at 500°F.

This low yield strength at 500°F would result in a weight savings over 18-8 stainless steel of less than 10 pct in the hot air ducts of the pneumatic system. Considering the problems involved it was decided that this small savings in weight would not warrant its use in this application.

Preliminary fabrication tests were run on the initial shipments of material. It was determined that some forming could be accomplished at room temperature, however, the wide range in properties of material from the two sources introduced inconsistencies. At 550°F these inconsistencies were somewhat overcome and formability approached that of 18-8 stainless steel at room temperature. Tests established that the material could be successfully fusion welded if adequately shielded by inert atmosphere on both top and bottom surfaces. Means of providing an adequate gas backing could at times present a difficult problem, depending upon the geometry and accessibility of the weld joint. Spotwelding of the material was readily accomplished in the received condition providing the surfaces were properly cleaned with ½ pct hydrofluoric acid. The wide range of properties resulted in inconsistencies in spotweld strength. If the strength was over 100,000 psi the ratio of tensile to shear strength of the spotweld fell below 25 pct, which is considered the minimum indicative of good nugget ductility. The preliminary tests indicated that the wide spread in mechanical properties in sheet from the two sources could result in difficulties in fabrication practice and spotweld applications.

Boeing Material Specification BMS7-7a for *Commercially Pure Titanium Sheet and Strip* was prepared and coordinated with the two sources in an effort towards standardization. This specification required a tensile strength of 80,000 to 100,000 psi, a yield strength of 60,000 to 90,000 psi and 15 pct minimum elongation in 2 in. After gaining some production experience the two sources agreed to attempt to meet these requirements.

Near the end of 1950 appreciable quantities of the unalloyed titanium sheet were received from both sources. Some of the first sheets were far from flat and contained numerous imperfections. To use some of the first material it was necessary to selectively lay out parts to avoid these defects. The surface quality improved with each shipment until sheets comparable to annealed 18-8 stainless sheets with 2D finish were received. For test purposes a specimen was cut from each sheet received to determine mechanical properties, bending characteristics and chemical analysis. There have been 390 sheets received of gages from 0.016 to 0.062.

The results of tests on material produced to BMS7-7a from the two sources was reviewed. The material from source A showed a relatively wide distribution in properties, there being 15 pct of the specimens over the specified ultimate strength and 13 pct below that specified. The skewed appearance of the distribution curve indicates that there was some material with lower properties that was not shipped. The material from source B had a normal distribution curve that was somewhat narrower. The curve was displaced in relation to specified properties showing 17 pct of the specimens with properties over the maximum ultimate strength and less than 2 pct below minimum ultimate strength. The inconsistency in mechanical properties of commercially pure material from the different sources presents a problem. Larger ingots and continuous rolling will undoubtedly result in improved consistency within any one source but differences in production practices between sources may have to be further standardized.

The actual production parts of commercially pure titanium for two airplanes included over 500 part numbers and represented an approximate total quantity of over 3000 parts. It amounted to 650 lb per airplane and represents a saving in weight of approximately 430 lb. These titanium sheet metal parts were fabricated by the experimental tooling dept. on conventional equipment used in the production of aircraft parts. Figs. 1 to 5 show typical parts formed on various types of equipment.

The application of titanium alloy sheet to airframe construction has not progressed as rapidly as many would like to see it advance. This has been principally caused by difficulties encountered in changing from pilot plant melts to production conditions. Also, the properties of the presently available alloys limit their usability. The sheet alloys with which Boeing Airplane Co. has had limited experience because of availability are Rem-Cru's alloy 130A, an alloy of mixed alpha-beta structure and Titanium Metal Corp. of America's alloy 150B, an alloy of all beta structure.

The 130A alloy is a binary 8 pct Mn alloy. It was originally produced to a minimum yield strength of 130,000 psi but because of notch sensitivity at low temperature, production was held up on the material. It is again being offered with a minimum

Fig. 3—Stiffener lower cowl, upper part formed in rubber hydropress at 550°F with a steel hydroblock —5° spring back, lower part formed at room temperature —10° spring back, using 0.025 gage commercially pure titanium-condition "A".

guaranteed yield strength of 110,000 psi, an ultimate tensile strength of 120,000 psi and 15 pct elongation in 2 in., low temperature ductility having been bought at the expense of strength. Several sheets of 0.063 gage 130A alloy of the current analysis have been received. Typical room temperature properties are 144,000 psi ultimate, 130,000 psi yield and 15 pct elongation. At 500°F the short time tensile properties are 102,000 psi ultimate, 63,000 psi yield and 16 pct elongation.

Fusion welding tests run on the material have shown the welds to be extremely brittle and to date it has not been possible to restore the ductility. If the material was fusion weldable it would have considerable application in replacing stainless steel in welded parts. This alloy can be used to advantage in riveted structural applications where jet engines submerged in the fuselage heat the structure and thus make aluminum alloys unsuitable because of lower properties at elevated temperatures. The Boeing B-47 and B-52 airplanes have the jet engines suspended from the structure and therefore do not have this problem. It may also find application for the skin of supersonic aircraft.

The 150B alloy manufactured by Titanium Metals Corp. is a nonhardenable beta alloy of 5 pct Cr, 5 pct Fe and 5 pct Mo. It has somewhat of a weight disadvantage, being fairly highly alloyed with relatively heavy elements. The 150B alloy has a density of 0.189 lb per cu in. as against 0.163 lb per cu in. for pure titanium. It has been held back because of difficulties encountered in mill processing. The minimum guaranteed ultimate tensile strength is 140,000 psi, the yield strength is 120,000 psi and elongation is 10 pct in 2 in. The alloy is unstable above 400°F, becoming quite brittle when exposed to a temperature of 450°F for 800 hr.

One sheet of this alloy of 0.062 gage has been received by Boeing Airplane Co. Typical room temperature properties were 155,000 psi ultimate tensile strength, 149,000 psi yield strength and 11 pct elongation. Its operating temperature is limited to 400°F because of embrittlement. At that temperature it has short time tensile properties of 125,000 psi ultimate tensile strength, 118,000 psi yield and 15 pct elongation. Fusion welding tests run on the material have shown the weld to be very brittle. Methods tried in an endeavor to restore the ductility were unsuccessful. The minimum guaranteed strength for this material would not result in any weight savings over 75ST aluminum alloy at room temperature. It would show some advantage at about 300°F but cannot be used over 400°F. The Boeing structural development unit intends to run tests on built up structures of this alloy to investigate further its possible structural advantages.

Fig. 4—Channel lower cowl, formed in the drop hammer at 550°F by staging. For this part, 0.042 gage commercially pure titanium-condition "A", was used.

Fig. 5—Frame upper cowl formed by hot breaking the "2" section at 550°F, then stretch wrap forming the contour on the Cyril bath at room temperature, using 0.062 gage commercially pure titanium-condition "A".

The potential uses of titanium alloy sheet and strip in the airframe construction depends upon the development of stronger alloys with good fabricating characteristics. In subsonic aircraft, titanium alloy sheet in structural applications will be competing with the normal and low temperature properties of high strength aluminum alloy and heat treated low alloy steel.

An all purpose alloy to replace high strength aluminum alloy should have the formability of annealed 75S aluminum alloy and be capable of developing an ultimate tensile strength approaching 175,000 psi, a yield strength near 90 pct of that, and 10 to 15 pct elongation. It should be spotweldable. Fusion weldability would be desirable but not essential as high strength aluminum alloys are not considered fusion weldable. These properties would appear to require a heat treatable alloy. Appreciable quantities of 24S and 75S aluminum alloys are purchased in the age hardened condition and used flat or with only a minimum of forming. For this application a high strength titanium alloy would not necessarily have to possess good formability characteristics.

An alloy sheet with adequate ductility after welding, good formability at room or elevated temperature and an ultimate tensile strength of approximately 150,000 psi, a yield strength near 90 pct of that and 15 pct elongation in 2 in. would find considerable application. It could compete with low alloy steel heat treated to 180,000 to 200,000 psi in welded structure. It would replace stainless steel in welded applications where structural strength is required up to 800°F.

In supersonic airplanes where skin heating can be a factor, titanium alloy sheet in the vicinity of 150,000 psi tensile strength and 135,000 psi yield strength would be considered for use. It would be desirable for this material to have good formability and be spotweldable.

In missile design, fuel tanks are a factor. The corrosion resistance of presently available titanium alloy sheet appears to be satisfactory as does the strength, but the weld ductility is far from adequate. A weldable alloy of approximately 120,000 psi ultimate strength, 110,000 psi yield strength and 15 pct elongation in 2 in. would find considerable application for fuel tanks in missile design. The corrosion resistance to fuming nitric acid would have to approach that of commercially pure titanium. It would have to be capable of being deep drawn at room or at elevated temperatures.

Titanium alloy sheet meeting the requirements outlined would find appreciable usage in the aircraft industry.

Transformation Characteristics Of 3 Pct Al-5 Pct Cr Titanium Alloy

by Lee S. Busch

OVER the past several years the P. R. Mallory Co. and more recently the Mallory-Sharon Titanium Corp. have been engaged in the development of titanium alloys. Although many alloys were made and tested during these development stages, one alloy in particular has exhibited rather exceptional physical properties. This alloy contains normally 3 pct aluminum, 5 pct chromium, balance titanium.

The first alloy containing aluminum and chromium was made by powder metallurgy methods. At that time a fairly complete summary of the effect of various alloying ingredients on titanium was made. The promising results obtained on many alloys using these rather crude methods indicated that a melting process, if melting was accomplished without severe contamination, should furnish alloys which had interesting physical properties. A melting process was developed using graphite as the melting crucible which produced hundreds of 2 lb ingots with an average carbon content of 0.44 pct.

One of the first 3 pct Al-5 pct Cr-Ti alloy ingots made in this furnace had 177,300 psi ultimate strength with 6.25 pct elongation in 2 in. Heat treatments were attempted and it was found that a water quenched bar of this alloy was very brittle and hardened about four points R_A on quenching from 1000°C into water. Slow cooling from 900°C restored the hardness to the as forged level. These early alloys had tensile strengths of 170,000 to 190,000 psi as forged, with elongations of 5 to 7 pct. Impact values were about 5 ft-lb and the rotating beam fatigue strength of these early alloys was about 90,000 psi.

A great deal of work was done on the heat treatment of the 3 pct Al-5 pct Cr alloy. Quenching and drawing, using several schedules, were tried, as were quenching and reheating schedules and the reheating of forged bars to various temperatures and slow cooling. There was no consistent improvement of physical properties over the forged condition. The alloy was heat treatable but it was not possible to consistently improve the physical properties of the forged condition or reproduce physical properties from bar-to-bar with any single heat treatment. Since the forged properties, when good, indicated great promise, a continuing investigation of the forging technique was undertaken.

All early work was done on 2-lb ingots. A larger furnace using a graphite crucible to melt ingot sizes up to 500 lb was constructed. So much interest in titanium alloys in general and the 3 pct Al-5 pct Cr alloy in particular had been generated by published properties obtained on laboratory ingots that some sale of the material looked feasible. The properties of the alloy that interested prospective users were: 1—The high strength level with acceptable elongation; 2—high resistance to deformation at elevated temperature, and its stability; and 3—high fatigue strength.

In the larger furnace, several ingots weighing up to 200 lb were made. It became apparent that these larger ingot sizes would require different techniques in melting and forging if the physical properties obtained on 2-lb ingots, which were so promising, were to be realized. The carbon content doubled from 0.5 pct to around 1 pct but subsequently has been reduced to 0.6 pct max. The forging technique became even more critical because the large ingot diameters increased the reduction necessary to reach small finished sizes. In the forging of 9 in. diam ingots to sizes less than 1 in., tensile strengths would be abnormally high and elongations low. Heat treatment would restore the ductility but with a very sharp drop, as much as 50,000 psi, in ultimate strength.

A heat treatment which would reproduce properties at the desired level became even more necessary. When reasonably large quantities of material had been delivered to the field for test, a need for

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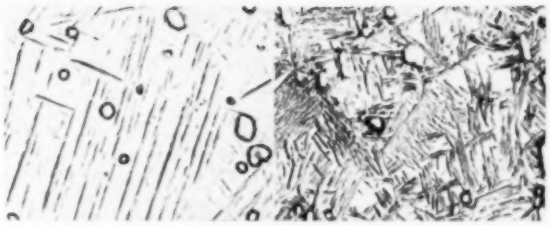

Fig. 1—Transformation structures for 3 Al-5 Cr-Ti alloy. Left, 1000°C—water quenched; right, 1000°C—lead bath quenched 825°C, held for 150 sec. X500.

information on other properties not directly measurable in laboratory tests became evident. Users were concerned with machinability, weldability, and other properties important in industrial fabrication. Forged sizes up to 7 in. diam requiring very high ultimate strengths were attempted but knowledge of forging technique was not adequate to produce the desired properties.

The search for a suitable heat treatment had been going on during all of the phases of the alloy development. In the absence of sufficient information on transformation kinetics, it became necessary to devise a forging technique which developed the proper microstructure during the forging operation. Using the forging technique devised after work on 30-lb ingots, it was possible to produce material with a minimum value of 150,000 psi ultimate strength and 6 pct elongation on section sizes up to 4 in. diam. One bar of this size had a tensile strength as high as 160,000 psi with 9 pct elongation. At these strength levels, machinability is still a problem. Forging technique must be carefully controlled and weldability was still an undetermined factor. Recently, welding information has been obtained which indicates that sound welds having typical tensile strengths can be made. The ductility of these welds is low, but proper heat treatment may improve them. It was apparent that a thorough knowledge of the transformation characteristics of the 3 pct Al-5 pct Cr alloy was an absolute necessity.

An investigation was set up to determine the effects of isothermal heat treatment on the following properties:

1—Physical properties in tension

2—Microstructure

3—Machinability—Though very low carbon content improves this quality, the effect of heat treatment on machinability should be known.

4—Weldability—Treatment of the weld metal, which may be sound and strong but which exhibits lower ductility than the base metal.

The effect of heat treatment on titanium alloy bars of $\frac{5}{8}$ in. diam has been determined. The effects of the heat treatment on machinability and weldability have yet to be determined. It is hoped that improvements in these qualities will be obtained.

Development of T-T-T Diagram

A time-temperature-transformation diagram was constructed for the MST 3 Al-5 Cr titanium alloy by New York University. Material from two ingots was used. The carbon content of one ingot was 0.51 pct and that of the other 0.78 pct. Specimens were homogenized in batches sealed in argon filled quartz capsules at 1000°C for 24 hr. Later work showed that samples homogenized at 1000°C for 30 min had the same beta grain size and hardness as samples homogenized for 24 and 40 hr.

Two specimens (one from each ingot), after the homogenizing treatment, were re-annealed in the beta plus carbide region in a helium atmosphere at 1000°C for 30 min. The samples were then quickly transferred to a lead bath and held there for a desired time, after which they were water quenched. Surface contamination of specimens could not be entirely avoided during homogenizing. Most of the samples revealed a thin surface layer of alpha phase, indicating contamination, and therefore the microstructures were studied after the contaminated layer was removed by grinding a section parallel to the axis of the original bars. Although no difference in microstructure could be determined between the inside of a specimen and the sample after the removal of the contaminated surface, it was necessary to remove about 0.01 in. of material before characteristic hardness values for a given heat treatment were obtained.

The heat treatments performed, as summarized in the T-T-T diagrams, show the temperatures and holding times in the lead bath and indicate the microstructures obtained. No appreciable differences were observed in microstructures or hardness values between samples containing 0.51 pct C and 0.78 pct C. Evidently the carbide phase does not influence the structures or hardness values in these studies within this carbon content range. However, a definite change occurred when the carbon content was reduced to 0.3 pct.

Transformation at 825° to 725°C

Specimens quenched in water show the structure characteristic of titanium martensites. The needles extend over the whole of the original beta grains and grain boundaries are not clearly visible. These transformation structures are shown in Fig. 1.

An identical microstructure was obtained in a specimen held in the lead bath at 825°C for 4 sec. On increasing the holding time at 825°C alpha platelets begin to precipitate. These alpha platelets precipitate at shorter time with decreasing temperature. The nucleation of alpha needles starts preferably at grain boundaries and at carbide-beta interfaces. The beta matrix untransformed at 775°C or 825°C transforms to martensite or alpha prime on quenching in water.

Alpha needles grow in bundles. Their crystallographic relation with the beta matrix is clearly

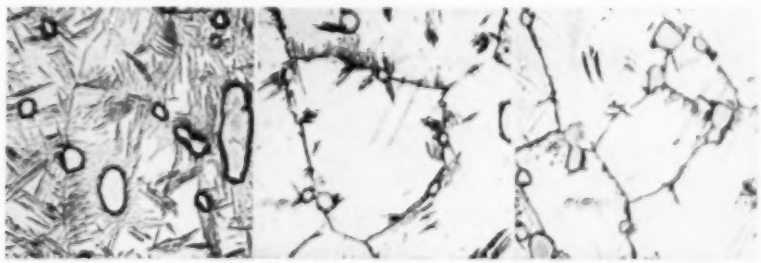

Fig. 2—Transformation structures for 3 Al-5 Cr-Ti alloy. 1000°C—lead bath quenched 780°C, held for various times. Left, 3 sec; center, 10 sec; right, 45 sec. X500.

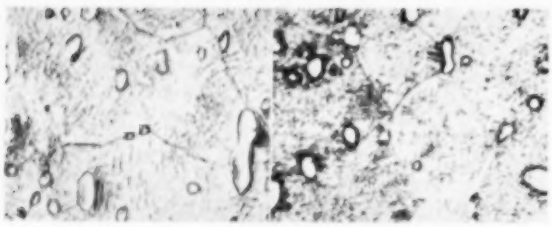

Fig. 3—Transformation structures for 3 Al-5 Cr-Ti alloy. 1000°C—lead bath quenched 720°C, held for various times. Left, 7 sec; right, 10 min. X500.

shown by the growth of alpha from the carbide-beta interfaces. Growth by diffusion proceeds mainly in the direction of the needles. At later stages, the needles increase in thickness probably by coalescence of two or more adjacent needles. Transformation in the 900° to 725°C temperature region takes place by nucleation and growth. A series of photomicrographs of samples isothermally quenched in this two-phase temperature range are shown in Fig. 2. All samples were electropolished and etched with Remington A etch or a solution of 1 pct hydrofluoric acid.

Transformation Below 725°C

A radical change in microstructure takes place at temperatures below 725° to 775°C. Specimens cooled from 1000° to 715°—725°C in the lead bath do not show large alpha platelets. The matrix of former beta grains consists of comparatively short thin needles in Widmanstätten arrangement which form quickly. A specimen held in the lead bath at 720°C for 6 sec reveals this structure fully developed. Longer times at 720°C seem to coarsen this structure only slightly, as shown in Fig. 3.

A study of the microstructure of a sample held for 2 sec at 670°C revealed that some grains formed fine short needles characteristic of this temperature whereas most grains developed martensitic structures on water quenching indicating that they were untransformed at 670°C. This type structure indicates that slightly more than 2 sec are required to cool the specimens from 1000° to 670°C. The Widmanstätten structure formed at 720°C is slightly coarser than that formed at 670°C after 6 sec.

It is probably significant that a distinct change in microstructure occurs in the interval between

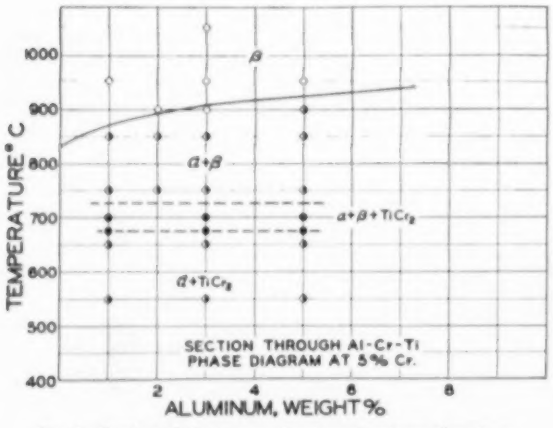

Fig. 4—Section of the ternary titanium-aluminum-chromium phase diagram. In the range 750° to 670°C beta begins to transform to fine alpha rather than alpha needles.

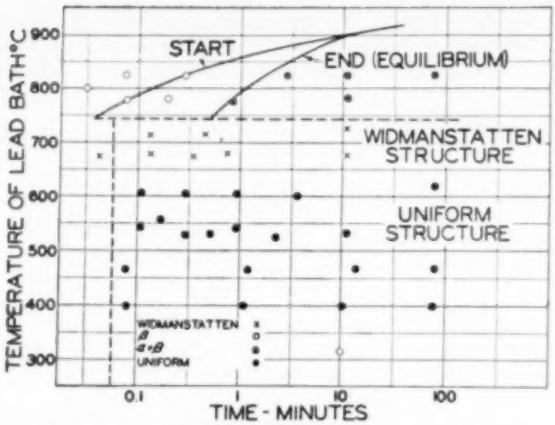

Fig. 5—T-T-T diagram determined at New York University. The lower temperature limit for the Widmanstatten region has not been definitely located.

750° and 670°C. According to previous work done at New York University, this temperature range corresponds to the three-phase alpha + beta + $TiCr_2$ field in the ternary titanium-aluminum-chromium phase diagram. Figs. 4 and 5 show the T-T-T diagram as determined by this work and a section of the ternary phase diagram. This suggests that the difference in microstructures produced between specimens transformed above and below 725°C may be attributed to the differences in rate of formation of alpha. It is in this range, 750° to 670°C, that the beta begins to transform to fine alpha rather than alpha needles. As the last beta transforms there is nucleation with very limited growth. The lower temperature limit for the Widmanstätten region in the T-T-T diagram has not been definitely located. The microstructures show a gradual increase in the fineness of the transformation structure as the temperature of the lead bath is lowered below 650°C.

Microstructures held in the lead bath below 600°C are so fine that only grain boundaries and carbide particles can be seen. Occasionally in some structures some needles can be seen at the boundaries and within the grains. Fig. 6 shows this after holding in the lead bath at 470°C for 5 sec.

Application of Transformation Curve to ⅝ in. Diam Test Bars

After the T-T-T curve had been determined on small specimens of approximately ½ in. diam x ⅛ in. thick, an attempt was made to give the same treatments to test bars ⅝ in. diam and approximately 4 in. long. Spot checks were made covering the entire T-T-T diagram. The general technique was the same as in the treatment of the small speci-

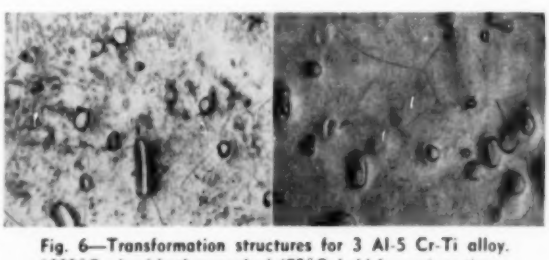

Fig. 6—Transformation structures for 3 Al-5 Cr-Ti alloy. 1000°C—lead bath quenched 470°C, held for various times. Left, 5 sec; right, 70 min. X500.

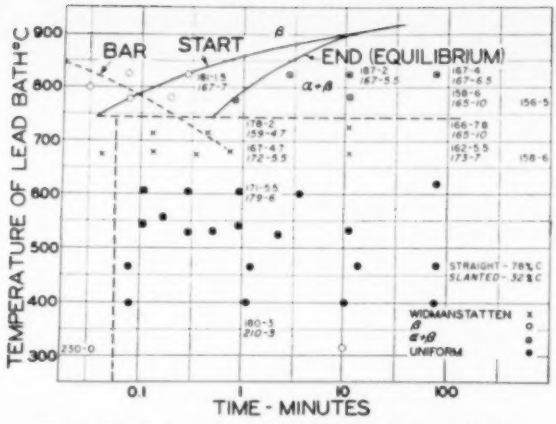

Fig. 7—T-T-T diagram shows ultimate tensile strength and elongation of ⅝ in. bars heated at 1000°C for 45 min and isothermally transformed in a lead bath from 825° to 340°C.

mens. The bars were heated at 1000°C for 45 min and then transferred to a lead bath for isothermal transformation at temperatures from 825° to 340°C. The ultimate tensile strength and elongation of these bars are seen on the T-T-T diagram in Fig. 7 at the location at which the transformation was terminated.

In working with ⅝ in. diam bars and comparing results with the small specimens microstructurally, the big difference occurs in the temperature range of 650° to 775°C. This is in the region of Widmanstätten structures. Below 650°C and above 775°C, the microstructures are the same on the ⅝ in. diam test bars as on the ½ in. diam x ⅛ in. thick specimens. This can be explained if one realizes that the low thermal conductivity of titanium permits the inside of the bar to remain at a higher temperature for a longer time with large cross sections than with the small specimens. Also, the structures are less time dependent in the low and high temperature regions.

Surface oxidation seems to further cut down the rate of heat transfer. The net result is to produce uniform structures across 2/3 of the cross-section while the outside edges differ microstructurally from the center. The degree of difference depends on the temperature (within the bar) at which transformation occurs.

In transforming a ⅝ in. diam bar at 700°C the structure will be more similar to a small specimen transformed at 750°C than a small specimen transformed at 700°C. Generally speaking, the bar behaves during transformation as if its center were at a higher temperature than the quenching medium. This is normal metallic behavior.

The bar cooling curve shown on the T-T-T diagram in Fig. 7, indicates the way a bar cools and the transformations that will take place. If bars are transformed in the upper portion of the Widmanstätten region, duplex structures result. The first transformation product to form, which nucleates at carbides and grain boundaries, is coarse alpha and is typical of transformation products occurring in the alpha-beta region. This surrounds areas which have the structure more typical of the temperature of the cooling medium which is an alpha prime structure as shown in Fig. 3.

Fig. 8 shows the effect of carbon on the microstructure and properties. Below 0.5 pct C, the elongation is definitely greater for a given treatment and the ultimate tensile strength is significantly higher than material containing 0.78 pct C. Recent evidence indicates a real difference in reaction to heat treatment. The structures of bars containing 0.3 pct C are finer and contain less acicular alpha than the high carbon bars. The solubility of carbon in titanium is 0.5 pct at 900°C and decreases with temperature. Therefore, the finding of differences between alloys which have been hot worked or heat treated in the 900° to 700°C range and contain percentages of carbon above and below the 0.5 pct figure is probably significant.

Conclusions

The construction of the time-temperature- transformation diagram for the 3 pct Al-5 pct Cr alloy has indicated the complexity of the transformation characteristics of the alpha-beta type titanium alloys. Results of tensile bars indicate that reproducible properties can be obtained from an isothermal treatment.

An isothermal heat treatment, typified by the following schedule, has been developed: Conversion to beta by heating for sufficient time above the beta transus to convert the alloy to the beta form (950° to 1000°C for 1 hr per in. of cross-section); and subsequent transformation of the beta structure at a temperature above room temperature and without cooling to room temperature. In the case of the Al-Cr alloy, this temperature would be in the region of 500° to 800°C depending upon section size.

Indications are that this heat treatment will give reproducible properties at a predetermined level on ⅝ in. diam test bars. Preliminary work indicates that this is also true of section sizes as large as 1 in. Work is progressing to determine the effectiveness of the heat treatment in sizes up to 6 in.

The effects of this heat treatment on machinability and weldability have yet to be determined. It is possible that machinability and weldability will be improved by use of the isothermal transformation technique.

Acknowledgments

The Mallory-Sharon Titanium Corp. wishes to thank the Navy Bureau of Aeronautics and New York University for their cooperation and assistance in developing the time-temperature-transformation curves and some of the microstructures presented herein.

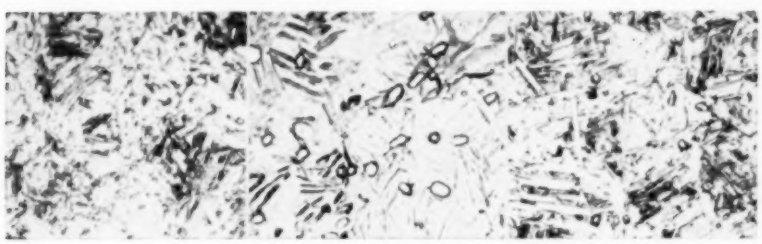

Fig. 8 — Effect of carbon and quenching medium on microstructure and physical properties. Left, 0.32 pct C, lead bath quenched—750°C, 165,300 psi ult tensile, 9.8 pct elong. Center, 0.78 pct C, lead bath quenched—760°C, 158,300 psi ult tensile, 6.2 pct elong. Right, 0.32 pct C, air quenched—700°C, 164,300 psi ult tensile, 9.4 pct elong.

Titanium Production and Fabrication At Republic Steel Corp.

by T. E. Perry

REPUBLIC is melting titanium by both arc and induction melting methods. Induction melting in graphite crucibles under inert gas atmospheres has been described in the literature. There have been no basic changes in induction melting. Graphite crucibles are still being used. The crucible material that will allow uncontaminated induction melting has not yet been found so the titanium melting industry has not yet been revolutionized. Basically, induction melting has a significant place in the producing industry, particularly in its relationship to scrap utilization. Its potential importance is forcefully seen in that from ingot to finished fabricated part, scrap losses of various types will run as high as 75 pct. The greatest part of this total cannot be economically remelted in the arc furnace at present. Most of it, however, could be remelted in the induction furnace into usable product. The continuous accumulation of high cost scrap is one of the most potent factors in future pricing schedules for all titanium mill product. The obvious answer to the problem is more promotion of induction titanium in the application where it can be used to advantage. High strength alloy bar and forging applications where ductility is of secondary importance suggest a large potential market. Other applications such as titanium castings should and undoubtedly will be developed for scrap utilization.

There are many modifications of the arc melting process, which essentially involves a continuous ingot buildup in chilled molds under inert gas or vacuum. Generally speaking, there is no standardized titanium arc melting furnace. Many modifications of the basic design are still being evaluated as regards product quality, ease of processing, and economies of melting. Uniformity of arc melted product has been one of the most significant problems. This problem stems essentially from sponge variation and the mechanics of melting and alloying. Republic has gradually come to accurate sponge segregation and the uniformity of alloys, the mechanics of alloying in the arc furnace, no longer constitute a major problem. The end effect of this progress will become apparent in smaller allowable spreads in physical properties on arc melted product.

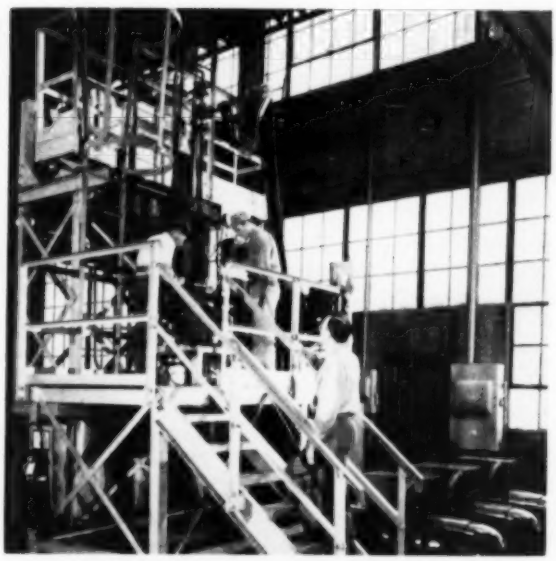

Fig. 1—When low carbon titanium is required, Republic employs arc melting. This is the No. 1 arc furnace in operation, melting titanium.

Sheet flatness remains a problem. However, commercially flat sheets are now adequate for most commercial fabrication.

Significant improvements in surface quality have been made primarily because of advances in mill processing techniques. Sheet sizes still are generally limited to about 36x96 in. and 0.018 is still a target minimum gage for both alloy and commercially pure sheets. Some relaxation of these limits is made for some applications. Melting capacities are quite flexible; at least it can be said that furnace design has reached the point where, upon relatively short notice, any required capacity can be made available within the limits of the sponge producing industry.

T. E. PERRY is with the Metallurgical Dept., Republic Steel Corp.

Commercially pure titanium is available in three grades: RS-40, RS-55 and RS-70. The reference is to yield strength level and the variation is caused primarily by purity level of sponge. These three grades offer a graduation of strength and ductility levels to meet varying fabrication and end usage needs.

RS-110 and RS-120 are commercial designations for alloy titanium, again, with reference to minimum yield strength in the annealed condition. RS-110 is a 6 pct FeCr grade, and RS-120 contains 7 pct Mn. Both alloy grades are amenable to a relatively wide range of physical properties by heat treatment. Increasing temperature and cooling rate increases hardness, yield and tensile strengths, but lowers ductility. The physical effects are attributed primarily to proportionment of the alpha and beta phases and their micro orientation in the structure. What appears to be precipitation aging is a second type of thermal treatment. Either grade when fast cooled from temperatures above about 1000°F and reheated to about 800°F will show pronounced aging phenomena. Quenching temperatures, cooling rate and subsequent holding time at 800°F are variables that can be controlled to give a wide range of physical properties. RS-120 forgings, of 1½ in. cross-section, for example, have been heat treated to 150,000 psi yield, 192,000 psi tensile, 22.4 pct reduction of area and 11.5 pct elongation, with the following thermal aging cycle: 1300°F, 2 hr-air cool, draw 800°F, 8 hr and again air cool.

If there be axioms in the fabrication of alloy titanium, the most important would be to keep grain size as fine as possible. This applies to forging, sheet fabrication, welding and related processing. If fabrication can be modified to give a fine, final grain size, much can be gained by subsequent thermal treatment. If grain size is lost, no thermal treatment can restore physical properties.

Much progress has been made in titanium alloy forging. It is known that with only slight modification of forging techniques, titanium can be made to fill the die and produce a physically acceptable forging. In most cases, however, further modification of practice for better grain size control is needed. Heat treatment as relating to finished forging size and shape needs more reproduction for true evaluation. Republic is anxious to work as closely as possible with the forging people in this respect since almost every forging job is presently a custom job and generalities are impossible.

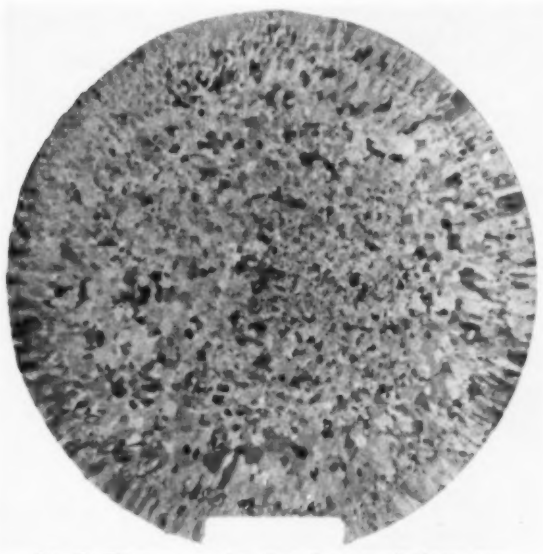

Fig. 2—This cross-section through arc melted titanium alloy ingot shows typical as-cast structure (reduced section) of 6 in. diam ingot. Ingots are skinned to a depth of about ⅛ in. prior to forging to remove the somewhat irregular skin.

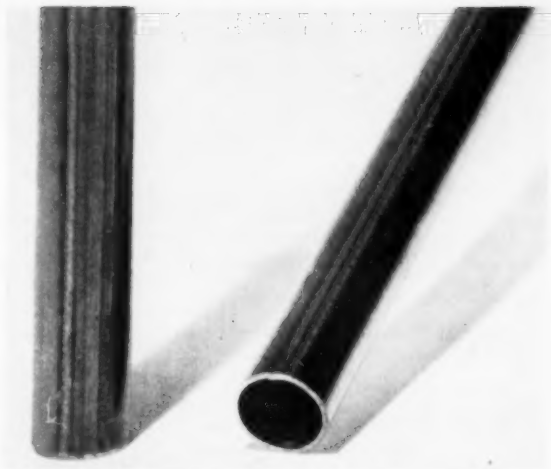

Fig. 3—Sections of 16 gage, commercially pure titanium tubing are shown, as-welded by the automatic inert gas arc welding process. In welding, it is important to keep both sides of the weld blanketed with inert gas to prevent atmospheric contamination.

New alloys are being developed which show much promise, however, because presently available alloys have not yet been completely evaluated, application of some of the more promising experimental alloys is still some time off. Welding of alloy grade titanium is still a major problem among many fabricators. Basically, the problem is one of grain size control in the weld and weld effect zones of present commercial alloys. It has been established that if welding techniques can be modified to permit a fine grain weld, required properties can probably be obtained by thermal treatment. There are several approaches to grain size control in making a weld and in cases where early techniques have been developed results appear to be quite promising. This particular problem should be the object of intense investigation and on presently available alloys.

The hypothesis that alloy grade sheets might be fabricated in a relatively soft condition and the finished part heat treated to higher physical properties has justly received much consideration, but complete evaluation of such a schedule remains to be completed.

In reviewing these few thoughts, it would appear that the most significant recent metallurgical developments of today are nothing more than evaluation of the more promising developments of yesterday. The pace has been extremely rapid and new developments are in constant demand from all sources. Still, evaluation is the key to production with both producers and consumers, and production usage is the key to cheaper product, broader fields of application, and continued development. The inertia alone of present research activities will carry a long way. This is as it should be. What is desperately needed now is more of the unglamourous evaluation of available products.

AIME Annual Meeting Program, February 16 to 19, 1953

Hotel Statler, Los Angeles

Names of Divisions and Subdivisions are coded as follows: MIED—Mineral Industry Education Div. MED—Mineral Economics Div. M—Mining Subdiv. G—Geology Subdiv. Geophys—Geophysics Subdiv. NM—(nonmetallics) Industrial Minerals Div. Coal—Coal Div. MBD—Minerals Beneficiation Div. EMD—Extractive Metallurgy Div. IMD—Institute of Metals Div. ISD—Iron & Steel Div. Petroleum Branch—Named as such. SEG—Society of Economic Geologists.

All technical sessions and other features of the annual meeting will be held in the Hotel Statler unless otherwise specified.

SATURDAY, FEBRUARY 14

10 am to 5 pm
Council of Section Delegates

SUNDAY, FEBRUARY 15

12 m
Student Relations Committee—Luncheon

2 pm
Board of Directors

2:30 pm
MIED—At Univ. So. Calif.

8 pm
IMD—Program Committee

MONDAY, FEBRUARY 16

8:30 am
Registration

9 am
ISD—*Blast Furnace*
Petroleum Branch—Executive Committee

9:30 am
Metals Branch Council

9:45 am to 12 m
MIED
M—*Special Mining Problems*
NM—*Chemical Raw Materials*
Coal—*Mining Western Coals*

10 am
IMD—*Constitutional Diagrams*
IMD—*Titanium Properties*

10:30 am
EMD—*Copper*
MBD—Business Meeting

12:15 pm
Welcoming Luncheon
Governor Dan Thornton, Speaker

2 pm
SEG, NM—*Dimension Stone*

2:30 pm
MED—*The Paley Report*
M—*New Mining Developments*
G, Geophys—*General Session*—Mayfair Hotel
NM—*Chemical Raw Materials*
Coal—*Preparation*
MBD—*Crushing and Grinding*
Petroleum Branch—*Production Review*
IMD—*Titanium Constitutional Diagrams*
IMD—*Plastic Deformation*
ISD, EMD—*Slags, Mattes, Etc.*
EMD—*Copper*
EMD—*Lead and Zinc*

Mining Branch Council

4 pm
IMD—*Membership Committee*

5:30 pm
Pre-Smoker Cocktail Party

7:30 pm
Dinner-Smoker

TUESDAY, FEBRUARY 17

8 am
EMD—Executive Committee
MBD—Scotch Breakfast

9 am to 10:30 am
ISD, EMD—*Slags, Mattes, Etc.*

9 am to 11:30 am
MED, EMD—*Aluminum, Magnesium*

9 am to 12 m
M—*Cost Cutting Developments*
G—*Application of Geology*, Biltmore Hotel
NM, SEG—*Rare Minerals*, Mayfair Hotel
Coal—*Utilization and Preparation*
IMD—*Metallography*
EMD—*Lead, Zinc, Antimony*
Student Session, Edison Auditorium
Petroleum Branch—*Technical Session*
MBD—*Materials Handling*
MBD, EMD—*Solids-Fluids Separation*

9:30 am
Women's Auxiliary Annual Meeting

10 am to 11:30 am
MGG—Executive Committee

10:45 am
ISD—Annual Business Meeting

11 am
Howe Memorial Lecture
by Joseph Winlock

12:15 pm
MGG—Luncheon—Mayfair Hotel
Coal—Luncheon
MIED—Luncheon
EMD—Physical Chemistry Committee Luncheon
IMD—Executive Committee Luncheon
Mining & Metallurgical Society of America—Luncheon

2 pm
M—*Stratified Mining*
G—*Lead, Zinc, Uranium Deposits*
NM—*Mineral Aggregates*
MBD, EMD—*Selection of Metallurgists*
MBD—*Solids-Fluids Separation*
Coal—*Mining, Handling Materials, Ventilation*
Petroleum Branch—*Valuation of Oil and Gas Properties*
IMD—*Research in Progress*
ISD, EMD—*Round Table—Slags, Mattes, Etc.*
EMD—*Aluminum*

2:30 pm
NM—*Ceramic Materials*
MED—Mayfair Hotel

4 pm
Annual Institute Business Meeting

5 pm
Directors Meeting, Executive

7 pm
Metals Branch—Dinner
Petroleum Branch—Dinner
Mining Branch—Dinner

9 pm
Informal Dance, AIME

WEDNESDAY, FEBRUARY 18

8 am
AIME Membership Committee
ISD—Executive Committee

9 am to 10:30 am
IMD—*Plastic Deformation*
ISD—*Gases in Steel*

9 am to 12 m
M—*Iron Mining*
G, Eng. Geol. Div., GSA—*Engineering Geology*, Mayfair Hotel
Geophys—*Aerogeophysics*
NM—*Mining Geology*
MBD—*Concentration*
Coal—*Mine Safety*
EMD—*Physical Chemistry*
EMD—*Copper Smelting*
EMD—*Titanium and Uncommon Metals*

9:30 am
Women's Auxiliary Round Table
Petroleum Branch—*Technical Session*

10:45 am
IMD—Annual Business Meeting

11 am
IMD Annual Lecture
by Kent R. Van Horn

12:15 pm
EMD—Luncheon
NM—Luncheon

1:30 to 5 pm
Petroleum Branch—*Technical Session*

2 pm
M—*Shaft Sinking Symposium*
G—*General Session*
Geophys—*Aerogyphics: Ground Geophysics*, Mayfair Hotel
NM, MBD—*Milling Methods*
MBD—*Operating Control*
MBD—*Flotation Theory*
Coal—*Mining*
IMD—*Mechanisms of Hardening of Alloys*
ISD—*Steel Production*
EMD—*Copper Smelting*
EMD—*Titanium and Uncommon Metals*

3 pm
AIME Nominating Committee

4:30 pm
NM—Executive Committee

7 pm
Annual Banquet
President's Reception

THURSDAY, FEBRUARY 19

9 am to 12 m
M, G
NM—*Industrial Minerals*
Geophys—*Geochemical Exploration*
MBD—*Mill Design and Construction*
IMD—*Creep in Metals*

10 am
Endowment Funds Committee

12:15 pm
MBD—Luncheon
IMD—Powder Metallurgy Committee Luncheon
Committee on Honorary Memberships Luncheon

2 pm
G, NM—*Nonmetallic Deposits*
Geophys—*Geochemical Exploration*
MBD—*Cleanup Session*
IMD—*Transformation and Thermodynamics*
IMD—*Structural Uses of Powder Metallurgical Parts*

Research In Progress

There is a vast amount of research work for both Government and private industry now underway in the industrial, Government, and university laboratories. JOURNAL OF METALS brings you a summary of some of the outstanding projects, with abstracts or summarizations of the progress thus far on such work, prepared by scientists in charge of the activities. Descriptions of these research projects will be given in greater detail at the AIME Annual Meeting, Hotel Statler, Los Angeles, at 2 pm Tuesday, Feb. 17, 1953. The papers will be presented in the same order as they appear here.

Partition of Some Alloying Elements Between Carbide and Ferrite in Steels

by D. A. Scott and G. S. Farnham

THE partition of alloying elements in a number of slowly cooled steels has been determined by analysis of electrolytically separated carbides, and the solutions obtained in the separation of these carbides. No significant amount of silicon was detected in the carbides. Of the other alloying elements present, 2.7 pct of the total nickel, 18 pct of the total manganese, 35 pct of the total chromium and 33 pct of the total molybdenum were found to be in the carbide, nickel and chromium content of the carbide being found to be a linear function of the amount of element present in the steel. The partition factor of a given element was not noticeably affected by the presence of other elements, although there was some evidence that the combined presence of chromium and molybdenum slightly reduced the amount of nickel in the carbide. An increase in the carbon content, while not affecting the nickel and manganese content of the carbide, did, because of the greater carbide weight, increase the partition factor for both alloying elements. Isothermal transformation and quench and draw experiments indicated that there was some replacement of nickel by manganese in carbides when steel was held at sub-critical temperatures.

D. A. SCOTT is Assistant Metallurgist, and G. S. FARNHAM is Assistant Manager, Canadian Development & Research, International Nickel Co. of Canada, Ltd., Toronto, Canada.

Rates of Diffusion and Marker Movements in Beta Brass

by U. S. Lundergren and R. F. Mehl

WHEN the measurements of marker movements accompanying diffusion in α-brass were published by Smigelskas and Kirkendall[1] six years ago, much speculation began as to the meaning of these results in the light of the possible mechanisms of diffusion in substitutional solid solutions. Da Silva and Mehl[2] subsequently found the phenomenon of marker displacement existing during diffusion in the

fcc α-phases of the systems Cu-Al, Cu-Sn, Cu-Ni, Ag-Au, and Cu-Au. It now seems clear on the basis of these observations that the mechanism of diffusion in fcc substitutional solid solutions is largely if not wholly of the vacancy type. Zener,[3] however, has shown that a type of atom interchange mechanism—specifically a 4-atom ring interchange—yields a much lower activation energy for the diffusion process than a direct atom exchange mechanism and suggests that this mechanism may be operating during diffusion in solutions with crystal structures other than fcc.

Accordingly it becomes interesting to determine whether marker movement—proof of the vacancy mechanism—may occur in lattices other than fcc. The diffusion process in the bcc β-phase of the Cu-Zn system was studied, employing pressure welded diffusion couples with 0.003 in. tungsten wires placed as markers at the interface. A definite marker displacement was found in all cases. As an example, it was found that for 52.5/40.2/52.5 atomic pct Zn type diffusion couples diffused at 750°C the marker shift, s (cm), varied with the diffusion time, t (hr), according to the equation:

$$s = 0.003 \times t^{1/2}.$$

This is a much larger marker shift than for a corresponding concentration difference in α-brass. It would therefore seem as though diffusion in bcc alloys, at least in β-brass, also occurs by a vacancy mechanism.

Diffusion in β-brass is quite rapid. The diffusion coefficient is a single-valued function of the concentration and varies from about 10^{-6} cm^2sec^{-1} at 800°C to about 10^{-7} cm^2sec^{-1} at 600°C for a 45 atomic pct Zn composition. The activation energy for the diffusion process is rather low: $Q_{av_g} = 17600$ cal $mole^{-1}$.

[1] A. D. Smigelskas and E. O. Kirkendall: *Trans.* AIME (1947) **171**, 130.
[2] L. C. C. da Silva and R. F. Mehl: *Trans.* AIME, (1951) **191**, 155.
[3] C. Zener: *Acta Cryst.* (1950) **3**, 346.

U. S. LANDERGREN and R. F. MEHL are associated with Carnegie Institute of Technology, Pittsburgh, Pa.

Residual Lattice Strains in Plastically Deformed Metals

by D. Rosenthal

THE production of residual lattice strains in polycrystalline materials under otherwise uniform external stress field, e.g. uniaxial tension, has been ascribed to various conditions of structural heterogeneity:

1—Existence of soft surface layers.

2—Interaction between boundary layer and crystalline interior of a grain.

3—Grain interaction.

Current X-ray diffraction work indicates that the third condition is probably the predominant one, at least in the following cases:

1—Removal of successive layers by etching an aluminum alloy and of surface layer by electrolytic polishing copper, failed to modify significantly the magnitude of residual strains—a circumstance which excludes the first condition.

2—Residual lattice strains in plastically deformed 25 Cr-20 Ni steel were found to vary with changing orientation of the X-ray beam in such a way as to imply the existence of a soft grain boundary in one case and a hard one in another, if condition 2 is assumed—a rather unlikely occurrence.

The hypothesis of grain interaction is free from the above shortcomings. However, the simple mechanism proposed originally by Greenough and based on Taylor's multiple slip theory, must be amended to account for the present results. The existence of deformation bands may be the reason for the observed discrepancy.

D. ROSENTHAL is associated with the Dept. of Engineering, University of California, Los Angeles. This work was partially sponsored by the University Research Committee.

Load Temperature History of Lattice Strain In Aluminum Alloy

by D. Rosenthal and M. Kaufman

THE variation of lattice strain in annealed 61S aluminum alloy under uniaxial tension was studied by means of X-ray diffraction technique up to 13½ pct plastic deformation at room temperature and 10½ pct plastic deformation at liquid nitrogen temperature. Observations were also made on speci-

mens loaded first at room temperature and then at liquid nitrogen temperature, or vice versa. Within the scatter of experimental data all results could be plotted on a single curve. However, measurements of residual lattice strains seem to indicate that this result may be due largely to the scatter of individual results, and that an equation of state no more exists for lattice strain than for plastic deformation.

D. ROSENTHAL and M. KAUFMAN are associated with the Dept. of Engineering, University of California, Los Angeles. This work was partially sponsored by the Naval Ordnance Test Station, Inyokern.

On Some Factors Influencing the Effect of Residual Stress in Fatigue

by George Sines and D. Rosenthal

PREVIOUS work has shown that the fatigue strength of notched aluminum alloy 61S-T6 can be appreciably raised by inducing compressive residual stresses at the notch. X-ray diffraction procedure was used to measure the residual stress and an analysis was devised to predict the effect of the residual stresses. Reasonable agreement with experiment was obtained. In the present work several characteristics of the notched part are discussed which have a bearing on the above analysis:

1—The ratio of yield stress to fatigue strength which is an index of the relief of residual stress by the fatigue load.

2—The influence of the static stress upon permissible range of alternating stress for the specific material.

3—The strength reduction of a notch and its dependence on shape and size of the part as well as microstructure of the material.

GEORGE SINES and D. ROSENTHAL are associated with the Dept. of Engineering, University of California, Los Angeles. This study has been partially sponsored by the NACA.

Intercrystalline Fracture and Twinning of Iron At Low Temperatures

by J. R. Low, Jr. and R. G. Feustel

IRONS containing 0.03 to 0.05 pct carbon normally exhibit considerable ductility and fracture by trans-crystalline cleavage when tested in tension at −195°C. After decarburization in moist hydrogen the same materials are completely brittle at −195°C and fracture occurs by inter-crystalline cleavage; recarburization restores the original properties and mode of fracture. Incomplete decarburization, which leaves the room temperature properties unaffected, leads to inter-crystalline fractures and brittleness at −195°C, however, the low temperature ductility and trans-crystalline mode of fracture may be restored by homogenization. In explanation of these results it is suggested that the grain boundaries in polycrystalline iron are surfaces of low cleavage strength, and that the resistance to cleavage of these surfaces may be greatly increased by the addition of small amounts of carbon.

It has frequently been proposed that the low temperature brittleness of iron may be caused by the formation of deformation twins at low temperatures. A number of observations on twinning in decarburized and carburized irons which were made in the course of this investigation are believed to demonstrate that twinning is a secondary phenomenon and cannot be considered as a cause of low temperature brittleness.

J. R. LOW, JR. and R. G. FEUSTEL are associated with Knolls Atomic Power Laboratory, General Electric Co., Schenectady, N. Y.

Dimension Effects and the Nature of Slip in Iron Sheet Single Crystals

by A. N. Holden and F. W. Kunz

AS part of a continuing study of the yield point phenomenon in carburized iron single crystals, this study was undertaken to better understand the previously reported effect of crystal dimensions on the yield point,[1] and to determine the nature of slip in those crystals which yield with a definite drop in load.

A good correlation between the length of the slip path as measured in the observed slip direction and the extent of the yield point phenomenon was obtained, with sharper load drops and greater yield point elongations being observed in the longer slip path crystals. Yield points were seldom observed when the slip path was less than 0.100 in. This effect is in agreement with dislocation models of yield point behavior.

Slip was observed to occur in highly localized deformation grooves in those iron crystals which showed a drop in load upon yielding. Slip directions seemed to be preserved in this mode of deformation since offsets were most pronounced in crystal surfaces normal to the predicted slip direction, but the grooves followed no definite plane. These grooves are considered to be for single crystals the equivalent of the Lüders bands found with polycrystalline steel.

[1] A. N. Holden: JOURNAL OF METALS, February 1952, 182.

A. N. HOLDEN and F. W. KUNZ are with Knolls Atomic Power Laboratory, Schenectady, N. Y.

Effect of Grain Size Upon Temper Brittleness

by D. C. Buffum and F. L. Carr

AN increase in austenitic grain size in SAE 3140 steel has been found to raise the temperature of transition from brittle to ductile failure, for tempered martensite in both temper brittle and unembrittled conditions. In addition, as previously suggested,[1] it increases the shift in transition temperature associated with temper brittleness. These findings hold even when the fine-grained and the coarse-grained material are quenched from the same temperature.

[1] A. Hurlich: Discussion to Herres and Lorig. *Trans.* ASM (1948) **40**, 805.

D. C. BUFFUM and F. L. CARR are associated with Watertown Arsenal, Watertown, Mass.

Effect of Microstructure Upon Temper Brittleness

by L. D. Jaffe

DETERMINATIONS of temperature of transition from brittle to ductile fracture of pearlite, tempered pearlite, and tempered martensite, in SAE 3140 steel, indicate that the pearlite does not become significantly temper brittle during its isothermal formation. In accord with previous findings,[1] the pearlite was less susceptible to temper brittleness than was tempered martensite.

[1] W. S. Pellini and B. R. Queneau: *Trans.* ASM (1947) **39**, 139.

L. D. JAFFE is associated with Watertown Arsenal, Watertown, Mass.

Accelerated Solidification in Ingots: Its Influence on Ingot Soundness

by Edgar Marburg

Most ingots complete solidification vertically rather than transversely. This conclusion is based on complete solidification patterns of big-end-up and big-end-down ingots developed from dumped and split ingots. New mechanisms for segregation in ingots are proposed. Internal soundness in ingots is found to depend upon adequate width of vertical core.

ALTHOUGH it has long been recognized that the internal soundness of ingots is principally dependent on the process of solidification, knowledge of this process is still only fragmentary. The mechanisms causing the several types of segregation in ingots, which mechanisms are necessarily related to the solidification process, are not well understood. In absence of a better conception of the solidification process, it seems hardly surprising that mold design varies widely. Guiding principles for mold design are needed. At stake in the improvement of ingot quality are not only improved properties of steel but also appreciably higher yields of sound steel, which would considerably decrease manufacturing costs.

In the present study, following a general description of the several types of segregation in ingots, Fig. 1, complete solidification patterns of a big-end-up and a big-end-down ingot, including the zones of accelerated solidification, have been reconstructed. In both ingots, a core of vertical solidification extends from the base cone to the hot-top junction. Based on the finding that ingots complete solidification vertically rather than transversely, as has been previously assumed, new mechanisms for segregation in ingots are proposed.

Internal soundness in ingots is found to depend upon the width of the vertical core, which in turn depends principally upon the width to height (w/h) ratio of the ingot. Solidification patterns of ingots are of three general types: 1—those in which vertical solidification does not reach the top, 2—those in which vertical solidification just reaches the top of the ingot, and 3—those in which vertical solidification reaches the top some time before transverse solidification would reach the middle of the ingot, so that a vertical core of definite width at the top of the ingot is developed. Axial defects vary characteristically with the solidification pattern. Examples of ingots of each type are presented.

Dumped ingot data reported by Nelson[1] have been used in developing families of curves of transverse and vertical solidification, and in deriving the effect of the w/h ratio upon the solidification pattern. Photographs of many ingots split at Homestead and at Duquesne Works, United States Steel Co., as well as those published by the British Iron and Steel Institute,[2] have been studied and analyzed. In the interest of brevity, only typical ingots of each type or classification from the above sources have been reproduced.

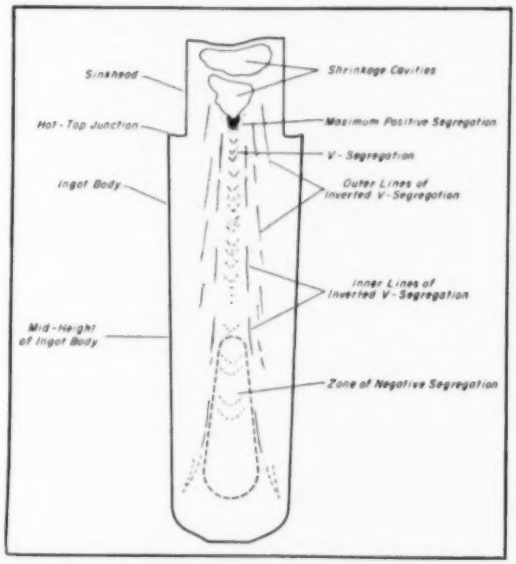

Fig. 1—Typical segregation pattern of a small ingot. Based upon sulphur print of Gary Works' 23x23 in. ingot.

Segregation in Ingots

Segregation in ingots falls into three principal classifications: 1—lamellar segregation, as revealed in sulphur prints (Figs. 2 and 3); 2—zone segregation, or broad variations in composition; and 3—interdendritic, or microsegregation. The last class, of minor importance, is not considered here.

When liquid metal cools, according to the theory of differential or selective solidification,[3] metal of relatively high purity selectively solidifies first. Liquid segregates (principally carbon, phosphorus,

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Fig. 2—Sulphur print of 23x23 in. ingot, AISI 1040 steel. Ladle analysis: C, 0.41 pct; Mn, 0.90; P, 0.016; S, 0.021; Si, 0.24. Ingot split at Gary Works.

Fig. 3—Sulphur print of 25x25 in. ingot, AISI 1040 steel. Ladle analysis: C, 0.45 pct; Mn, 0.71; P, 0.022; S, 0.037; and Si, 0.20. Ingot split at Homestead Works.

and sulphur) diffuse inwardly at definite rates.[7,8] But solidification also progresses at definite rates that decrease inwardly. Hence segregation does not extend far into the liquid, but is restricted to a narrow layer of liquid metal immediately adjacent to the face of solidification.[7,8] The width of this layer and its concentration of segregation increase inwardly. The several types of segregation in ingots and prevalent theories as to their mechanisms are discussed briefly below.

V Segregation: V segregation, Fig. 1, is a lamellar type of segregation revealed on sulphur prints as imperfectly developed V's centered on the vertical axis. Generally of maximum intensity in the upper portion of an ingot, V segregation may extend well below mid-height, Fig. 3. Ingots of intermediate sizes (15 to 25-in. width) are more subject to this defect than are either smaller or larger ingots. V segregation is less pronounced in big-end-up (Fig. 2) than in big-end-down (Fig. 3) ingots. In large ingots, V segregation occurs normally well below the hot-top junction, separated from the latter by a zone of clean sound steel, Fig. 4.

The mechanism proposed by the Heterogeneity Sub-Committee of the British Iron and Steel Institute[9]—that, in the final stages of solidification, the contraction of the ingot causes segregates to be

Fig. 4—Sulphur print of 52 in. diam ingot, AISI 1040 steel. Ladle analysis: C, 0.45 pct; Mn, 0.66; P, 0.019; S, 0.029; Si, 0.21. Ingot split at Homestead Works.

drawn downwardly from the sinkhead—fails to account for the clean zone mentioned above. Nor does it afford an explanation of the lamellar arrangement of V segregation.

Hultgren[4] suggests that V segregation results from the entrapment of segregated liquid metal between dendrites in the completion of solidification transversely. In absence of refill metal in final stages of solidification, the unsupported dendrites sag. Sagging plus contraction in cooling, according to Hultgren, cause the V shape of axial segregation. As applied to ingots that do complete solidification transversely (Figs. 22a and 23a), this explanation appears to be sound. As will be discussed later, however, it is not applicable to ingots that complete solidification vertically.

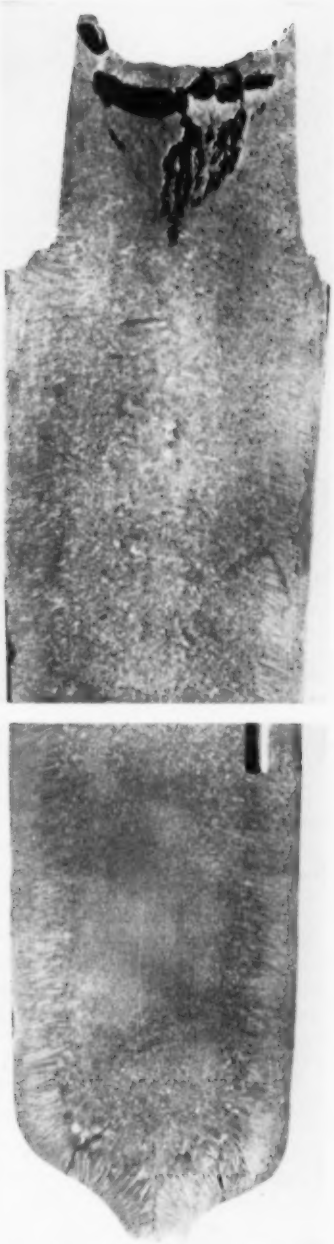
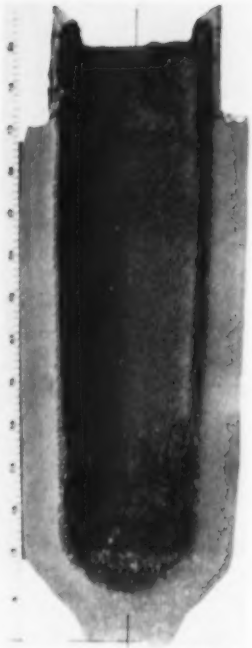


Fig. 5—Macroetch of 27x46 in. ingot, type 347 stainless steel. Ladle analysis: C, 0.08 pct; Mn, 1.26; P, 0.023; S, 0.013; Si, 0.28; Cu, 0.10; Ni, 11.18; Cr, 18.2; Cb, 0.80. Ingot cast at Duquesne Works, rejected on account of hanger cracks, split at Homestead Works.

Negative Segregation: In a roughly cone-shaped zone in the lower middle portion of ingots (Fig. 1), segregating elements occur in less than average concentrations. This region is referred to as the zone of negative segregation. The deficiency in segregating elements decreases upwardly to approximately mid-height in an ingot, at which level the steel attains an average or ladle composition.

As segregation normally increases inwardly, the zone of negative segregation in ingot interiors has been difficult to explain. In an attempt to do so, the



a—Ingot No. 1 dumped 34 min after pour.

b—Ingot No. 2 dumped 56 min after pour.

Fig. 6—Shells of 32x32 in. ingots dumped at various time intervals after pour. Ladle analysis: C, 0.83 pct; Mn, 0.77; P, 0.014; S, 0.024; Si, 0.18; Ni, 2.08; Cr, 0.15. Ingots split at Homestead Works.

a—Ingot No. 3 dumped 73 min after pour.

b—Ingot No. 4 dumped 94 min after pour.

Fig. 7—Shells of 32x32 in. ingots dumped at various time intervals after pour. Ladle analysis: C, 0.83 pct; Mn, 0.77; P, 0.014; S, 0.024; Si, 0.18; Ni, 2.08; Cr, 0.15. Ingots split at Homestead Works.

theory of random nucleation of crystals was proposed speculatively.[2] According to the random-nucleation theory, crystallites of high purity nucleate, or generate, in the liquid metal in the interior of an ingot. Being of greater density than the surrounding liquid metal, these crystallites purportedly descend to build up a zone of high-purity metal in the lower middle portion of an ingot.

Several considerations make acceptance of the theory of random nucleation of crystals difficult. First, the liquid metal in an ingot quickly attains the liquidus temperature and remains at this temperature until just before solidification occurs, when it drops sharply.[5, 7, 8] Second, according to Stokes' law, the rates of descent of crystallites in liquid metal would be so slow that they could not descend the required distance in the available time.[6] Third, macroetches of ingots show no evidence of a cone of crystals caused by the piling up of descending crystallites. In the 29x66-in. semikilled ingot (Fig. 17), for example, the equiaxed crystals are restricted to a well-defined vertical core above the base cone. If crystals descend in the liquid metal, crystals in the lower middle portion of an ingot should be larger than those above; the reverse is typical, Fig. 5.

In a re-appraisal of their theories some years after they were first proposed, the Sub-Committee on the Heterogeneity of Steel Ingots of the British Iron and Steel Institute held it more probable that the zone of negative segregation occurred as a result of ascent of less pure components away from it than that it was caused by the descent of high-purity crystals into it.[6]

Inverted-V Segregation: Inverted-V segregation is also a lamellar type of segregation, which appears in split ingots as one or a series of discontinuous lines outside the V segregation, Figs. 1 to 4. The lines incline slightly toward the vertical axis in an upward direction. Although lines of inverted-V segregation normally increase in number with in-

a—Ingot No. 5 dumped 118 min after pour.

b—Ingot No. 6 dumped 150 min after pour.

Fig. 8—Shells of 32x32 in. ingots dumped at various time intervals after pour. Ladle analysis: C, 0.83 pct; Mn, 0.77; P, 0.014; S, 0.024; Si, 0.18; Ni, 2.08; Cr, 0.15. Ingots split at Homestead Works.

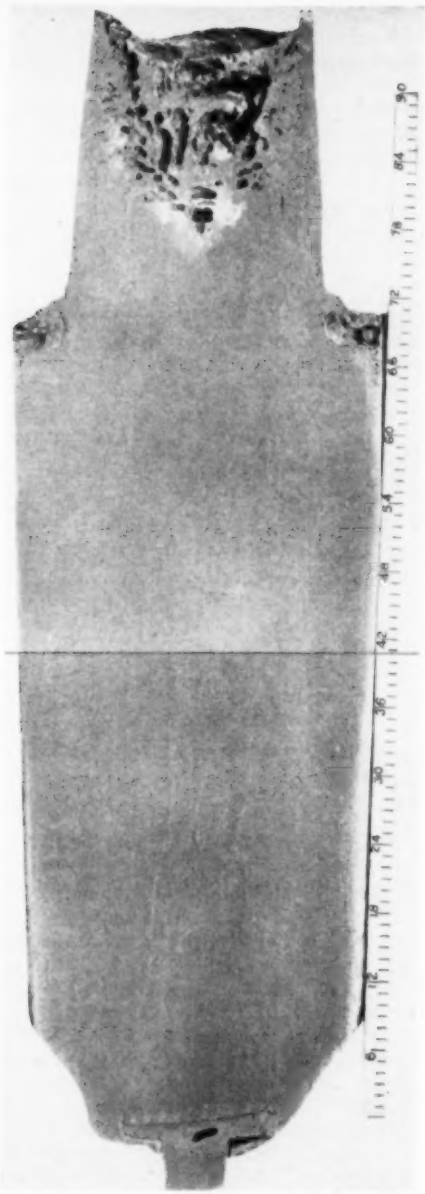


Fig. 9—Macroetch of 32x32 in. ingot, AISI 1020 steel. Ladle analysis: C, 0.22 pct; Mn, 0.52; P, 0.020; S, 0.037; Si, 0.29. Ingot split at Homestead Works.

crease of ingot size, their intensity, unlike that of V segregation, does not vary greatly. In large ingots they flare outwardly near the top to form a bottleneck, Figs. 4 and 24 to 26. In ingots in which such a bottleneck occurs, V segregation is restricted to the region just below the bottleneck, Fig. 4. For present purposes, lines of inverted-V segregation have been differentiated as to whether they are inner or outer lines, Fig. 1.

No satisfactory explanation of inverted-V segregation is found in the literature. According to one theory,[7] it results from the ascent of segregates along the face of solidification. Another[8] envisages periodic descent of crystallites, which causes segregates to be swept upwardly in successive waves.

The view is sometimes expressed that lines of inverted-V segregation are internal cracks resulting from cooling stresses. Examinations of fractured ingots at Homestead Works, United States Steel Co., have shown that these "lines" are actually narrow zones containing a network of fine dendrites, which indicates that layers of liquid metal were entrapped and solidified with an insufficiency of refill metal. To have been entrapped as a liquid, the metal must have had a lower temperature of solidification than the surrounding metal; that is, it must have been segregated.

Experimental Dumping of Big-End-Up Ingots

In experiments conducted under the supervision of the Metallurgical Department at Homestead Works, six 32x32-in. big-end-up ingots of 2 pct Ni steel were dumped at various intervals from 34 to 150 min after pour. Photographs of the split ingots appear in Figs. 6 to 8. The ladle analysis of the steel was: C, 0.83 pct; Mn, 0.77; P, 0.014; S, 0.024; Si, 0.18; Ni, 2.08; and Cr, 0.15.

The tapping temperature was 2885°F, the pouring temperature 2730° to 2680°F. The mold temperatures were not measured but were reported to be within the range (300° to 400°F) used in normal practice at Homestead Works. The mean mold-wall thickness was 7.75 in., which includes one-third depth of $\frac{3}{4}$-in. corrugation. Measurements of thickness were made from the outside of corrugations to the depth completely solidified. This is a close approximation of the depth from the centroidal plane of the corrugations to the mean depth of partially solidified metal at the face of solidification.

No completely solid ingot of the above composition was split. In Fig. 9 is a macroetch of an ingot of this size of 1020 steel.

Transverse Solidification: The depths of solidification as measured in the upper portions of ingot Nos. 1 to 5 (Figs. 6 to 8), which portions are of uniform thickness, are tabulated and plotted in Fig. 10. The equation of a straight-line representation of the five points is $d = -0.50 + 0.93\sqrt{t}$, where d is the depth in inches and t the time in minutes. Thus, initial transverse solidification occurred according

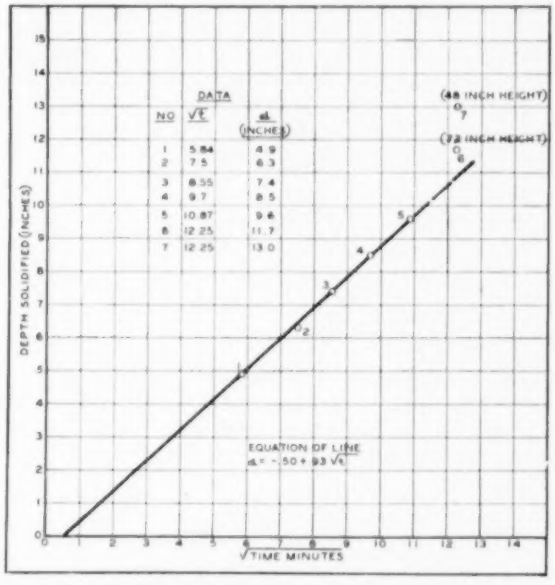


Fig. 10—Transverse solidification in Homestead Works' 32x32 in. ingot.

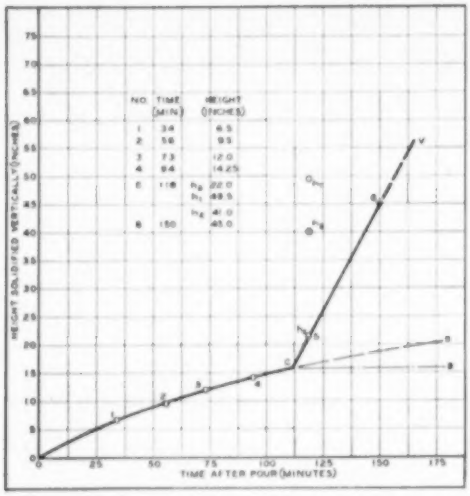


Fig. 11—Vertical solidification in Homestead Works' 32x32 in. ingot.

to the Chipman-FonDersmith equation,[10] $d = -C + k\sqrt{t}$.*

* This equation is a modification of Feild's equation, $d = k\sqrt{t}$.[11] The negative constant, $-C$, signifies that the curve intersects the abscissa to the right of the origin of coordinates. Dumped ingot data[1,10,12] (Fig. 10) support the Chipman-FonDersmith equation. Experimental data presented by Bishop, Brandt, and Pellini[7] indicate that the negative constant in the Chipman-FonDersmith equation increases with superheat.

The face of solidification on the right-hand side of ingot No. 6, Fig. 8b, is not parallel to the side of the ingot. This is evidence of accelerated transverse solidification, which will be discussed later. The depths of solidification at 48 and 72-in. heights in ingot No. 6 have been plotted, Fig. 10.

Vertical Solidification: To allow for the zone of partial solidification, ½ in. has been added to measured heights of complete solidification vertically. The assumed face of vertical solidification in ingot No. 6, which face was gouged by the burning flame, has been represented by a dashed line, Fig. 8b. The measured heights of vertical solidification in all of the ingots are tabulated and plotted in Fig. 11.

The secondary cavity between h_1 and h_2 in ingot No. 5 and the extensive porous zone below this cavity are clearly abnormal. Excessive jarring of the ingot during overturning may have resulted in flash solidification of the liquid metal.** It remained to

** Similar flash solidification has been observed in the interiors of small laboratory ingots that have been jarred excessively in overturning.

decide which height to measure: 1—the base of the wide cavity, h_1; 2—that of the narrow cavity, h_2; or 3—the height, h_3, of completely solid metal. As the last point, h_3, conforms with the pattern established by the other four points, Fig. 11, much more reasonably than does either of the other two points, it was used.

The completed curve of vertical solidification, *OCV* (Fig. 11), then, consists of two portions, *OC* and *CV*, the two intersecting at a wide angle *VCD*. The significance of this shape will be discussed later.

Effect of Ingot Width on Rates of Transverse and Vertical Solidification

Nelson[1] reported data from dumped 13x13 and 17x17-in. ingots of high-carbon electric furnace steel cast in molds of slightly less and slightly greater than 4-in. mean wall-thickness, respectively. Nelson's data for transverse and vertical solidification are related below to those for the 32x32-in. ingot.

Transverse Solidification: Based upon replots of Nelson's data, the following equations for initial transverse solidification have been derived: for the 13x13-in. ingot, $d = -0.50 + 1.2\sqrt{t}$; for the 17x17-in. ingot, $d = -0.10 + 1.04\sqrt{t}$. The parabolas of initial transverse solidification for these two ingots and that for the 32x32-in. ingot have been plotted in Fig. 12.† The plot indicates that the k value of initial transverse solidification varies inversely with ingot width. The reason for this may be considered.

† As the negative constant in the Chipman-FonDersmith equation is believed to vary with superheat, the same constant, −0.10, was used in all three equations from which the curves were plotted.

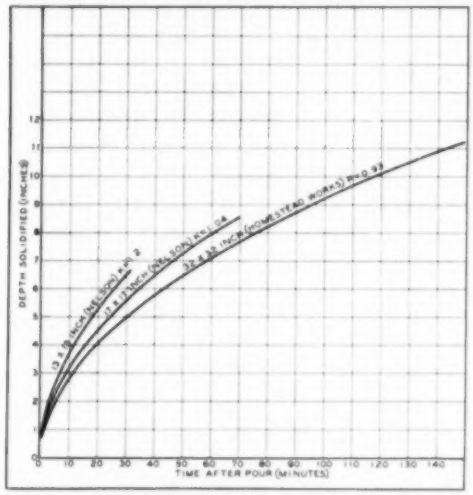


Fig. 12—Effect of ingot width on initial transverse solidification.

Temperature gradients established in mold walls from the middles of the hot sides to the less hot corners affect the k value for solidification across the middle plane. As ingot width decreases, the corner chills become increasingly effective. Thus k varies inversely with ingot width. As ingot width increases above some limiting width, perhaps 35 to 40 in., however, mold corners exert no further influence on heat extraction at the middle plane; that is, the normal k value for a given wall thickness is attained.

In addition to ingot width, mold-wall thickness influences k. Experimental data reported by Bishop, Brandt, and Pellini[7] indicate that k increases with increase of mold-wall thickness from 1½ to 4⅛ in. Data reported by Nelson[1] indicate that k increases with increase of wall thickness from 4¼ to 6¼ in. It seems not improbable that k would increase with further increase of wall thickness up to the maximum thickness used for mold walls.

In mold design, wall thickness is commonly increased with increase of ingot width. Hence the effect of the latter upon k is somewhat moderated by the opposite effect of the former factor. As both influences are reflected in the plotted curves (Fig. 12), however, the k values for transverse solidification of ingots of widths intermediate between 13 and 32 in. may be determined approximately by interpolation between the curves for these two ingots.

Vertical Solidification: Nelson's data for vertical solidification in his 13x13 and 17x17-in. ingots have been replotted on the same chart (Fig. 13), on which has been reproduced also the curve for the

32x32-in. ingot, Fig. 11. As in the last curve, the last plotted point for each of Nelson's ingots lies well above the initial curve through the first three points. Accelerated vertical solidification in the 13x13-in. ingot has been represented as a straight line through the last two points, the slope of which line is the minimum consistent with the data. A pattern for vertical solidification curves clearly emerges. The slope of the line through the last observed point for the 17x17-in. ingot has been determined by interpolation between the final curves for the 13x13 and 32x32-in. ingots. Complete vertical solidification curves for 20x20, 25x25, and 30x30-in. ingots, shown as dashed lines, have been developed similarly by interpolation between the curves for the above two ingots. The slopes of the final portions of the curves are uncertain; they may decrease upwardly a variable amount depending on segregation in ingot interiors.

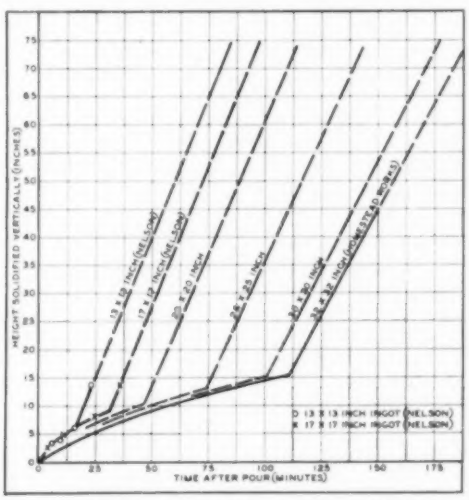


Fig. 13—Effect of ingot width on vertical solidification.

From Fig. 13, vertical solidification curves are apparently composed of two portions: an initial curve approximating a parabola and a final curve of steep slope. The two portions intersect at a height equal to approximately one-half the base width of ingot. The slopes of both portions decrease with increase of ingot width.

Accelerated Solidification in Ingots

As long as heat extraction is unidirectional, that is, all components are parallel, solidification follows the Chipman-FonDersmith equation, $d = -C + k\sqrt{t}$. When components of heat extraction occur in more than one direction, solidification, for the purposes of this paper, is said to be accelerated. Accordingly, solidification from curved surfaces and from ingot corners proceeds at accelerated rates from the start. The face of accelerated solidification widens as it proceeds inwardly in ingots to form zones of accelerated solidification. The zones originating at both side and base corners of ingots are considered below.

Accelerated Transverse Solidification from Side Corners: Nelson[1] noted that the faces of the cavities of 17x17-in. ingots dumped later than 20 min after pour were completely curved; that is, the faces of accelerated solidification arising at the corners had reached the middle planes. With a k value of 1.04 for the latter ingot, solidification would attain a

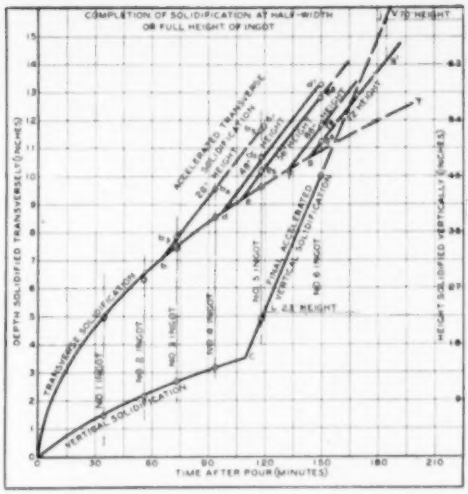


Fig. 14—Solidification curves for Homestead Works' 32x32 in. ingot.

depth of about 4½ in., or approximately one-fourth the face width, in 20 min. This proportionality of depth to face width may be expected to apply approximately to all square and rectangular ingots. Plotted dumped ingot data[1, 10] (Fig. 10), however, fail to show any appreciable acceleration at such depths. It may be concluded, therefore, that acceleration of transverse solidification caused by components of heat extraction to adjacent sides is too slight to be noticeable at the middle planes of ingots of commercial sizes.††

†† In small laboratory ingots, acceleration of this type may be quite significant.

Initial Accelerated Vertical Solidification: Analogous to the above, accelerated vertical solidification from base corners may be expected to reach the vertical axis at a height equal to about one-fourth the base width. Evidence that it does is found in the macroetch of Homestead Works' 29x66-in. ingot, Fig. 17. Above line *ada* vertical columnar crystals slope inwardly, which indicates that transverse components of heat extraction became effective along this line. The height, d, at which accelerated vertical solidification reaches the vertical axis is about 7 in., or about one-fourth the base width. Zone *adac* (Fig. 17), the upper portion of base cone *aca*, is therefore the zone of initial accelerated vertical solidification.

Vertical solidification from the rounded bases of big-end-up ingots occurs at accelerated rates from the start. If, for example, the data for the first four 32x32-in. ingots (Fig. 11) be plotted on a $d/\sqrt{t}$ basis, the resulting curve increases in slope inwardly. Such a curvature denotes accelerated solidification (the plot of unaccelerated solidification on a $d/\sqrt{t}$ basis is a straight line, Fig. 10).

Accelerated Transverse Solidification from Base Corners: Of much more practical importance than either of these two types of accelerated solidification is accelerated transverse solidification originating at base corners (*a* in Fig. 18) of big-end-down ingots, or at the points of tangency between the straight sides and the rounded bases of big-end-up ingots (*a* in Fig. 15). The loci of this acceleration, *ag* (Figs. 15 and 18), and its effects upon ingot soundness, will be discussed later.

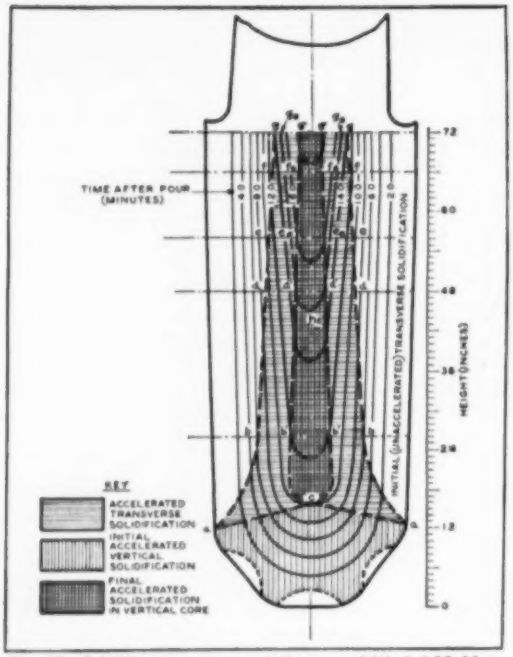


Fig. 15—Solidification pattern of Homestead Works' 32x32 in. big-end-up ingot.

Final Accelerated Vertical Solidification: Analogous to base cone *aca* (Fig. 17), as outlined by crystal structure in Homestead Works' 29x66-in. ingot, so-called base cones of vertical solidification *aca* (Fig. 15) are developed in big-end-up ingots. The height of the base cone is about one-half the base width of an ingot, Figs. 15 and 17. As this is also the height at which sharp acceleration of vertical solidification occurs (Fig. 13), a clue is provided as to the cause of this acceleration. At the tip of the base cone, the faces of transverse solidification from opposite sides first meet at the vertical axis, Figs. 15 and 18. Hence transverse components of heat extraction are here added to the vertical components. The added transverse components appear to be responsible for the high rates of final accelerated vertical solidification.

It has been generally assumed that vertical solidification is confined to the base cones of ingots. In the following, it is hoped to show: 1—that vertical solidification extends above the base cone in most ingots, and 2—that its extent is the determinant of the axial soundness of ingots.

Solidification Pattern of Big-End-Up Ingot: To aid in the development of the solidification pattern of Homestead Works' 32x32-in. ingot, the curves of transverse (Fig. 10) and vertical (Fig. 11) solidification of this ingot have been placed on the same chart (Fig. 14) to the same time scale but to different dimensional scales. The vertical scales have been adjusted so that one-half the top width, 16 in., on the left-hand scale for transverse solidification equals the full height of the ingot, 72 in., on the right-hand scale for vertical solidification. The direction in which solidification is completed, then, is determined according to which curve first attains the top horizontal line denoting completion of solidification in either direction. The curve of vertical solidification, *OCV*, reaches 72-in. height at *V* at about 187 min after pour; the curve of transverse solidification, *OT*, would not reach the same horizontal line, representing 16-in. depth, until much later; that is, solidification of this ingot was completed vertically rather than transversely.

Accelerated Transverse Solidification: Fig. 14 also shows curves of accelerated transverse solidification, plotted from data obtained from the dumped ingots, Figs. 6 to 8. For example, points b_3 and b_4 represent the wall thicknesses at 26-in. height as measured in ingots Nos. 3 and 4, Fig. 7. A straight line through these points intercepts parabola *OT* at point *b;* that is, accelerated solidification at 26-in. height began at about 7-in. depth and 66 min after pour.

Similarly, points e_3 and e_4 in Fig. 14 represent wall thicknesses as measured at 56-in. height in ingots Nos. 5 and 6, Fig. 8. Line e_3e_4 through these points is approximately parallel to line b_3b_4, and intersects parabola *OT* at *e*. Points *b* and *e* have been plotted on the solidification pattern of the 32x32-in. ingot in Fig. 15. Points *b* and *e*, plotted similarly on the split ingots, Figs. 7 and 8, lie on or in line with inner lines of inverted-V segregation, Fig. 1. These coincidences suggest that inner lines of inverted-V segregation are loci of acceleration of transverse solidification from base corners. Additional evidence to this effect is provided by Homestead Works' 29x66-in. ingot. Inner lines *ag* in the sulphur print, Fig. 16, have been reproduced as dashed lines *ag* in the macroetch, Fig. 17. The increased width of columnar crystals beyond these lines and their increased upward slope, particularly in the lower portion of the ingot, are indicative of added vertical components of heat extraction.

In addition to the evidence given, there appears to be a logical reason for the coincidence of inner lines of inverted-V segregation and acceleration of transverse solidification. As solidification rates decrease inwardly, the layer of liquid segregated metal adjacent to the face of solidification increases in concentration.[2, 5] Conversely, when solidification rates accelerate, the concentration of this segregated layer must decrease. The excess segregation above that which can be carried at the higher rates is, therefore, deposited where the rates increase.

In further support of the coincidence of inner lines of inverted-V segregation and acceleration of transverse solidification, inner lines invariably point to the base corners of big-end-down ingots (Figs. 3, 4, and 24 to 26), whence accelerated solidification proceeds.

In view of the above evidence, inner lines of inverted-V segregation have been utilized as loci of accelerated transverse solidification in the construction of the solidification pattern of the 32x32-in. ingot. Thus the depths of the inner line of inverted-V segregation, as measured to points *d*, *f*, and *g* in Fig. 8b at 48, 66, and 72-in. heights, respectively, on the right-hand side of ingot No. 6, have been plotted on both parabola *OT* in Fig. 14 and the solidification pattern in Fig. 15. The depths of solidification to points *d'*, f_6, and g_6 at the above heights in ingot No. 6 in Fig. 8b have also been plotted on both the solidification chart and pattern. Through these points have been constructed lines *dd'*, ff_6, and gg_6, representing accelerated solidification at the above heights, Fig. 14. These lines are approximately parallel with lines bb_3 and ee_4, previously developed. Accelerated solidification is thus revealed as progressing upwardly in the ingot from the base to the top, its rates not varying greatly. Lines *ag*, Fig. 15, constructed through points *b*, *d*, *e*, *f*, and *g*, then, are loci of acceleration of transverse solidification.

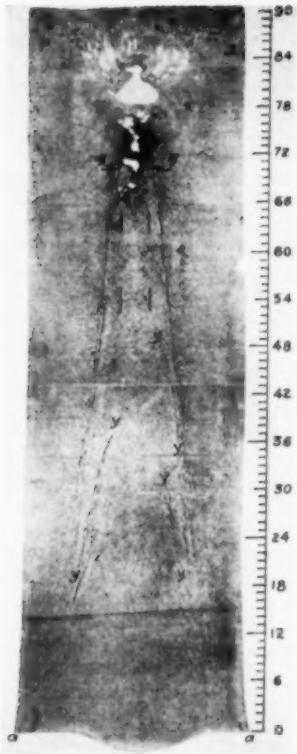


Fig. 16—Sulphur print of 29x66 in. ingot, semikilled steel. Ladle analysis: C, 0.24 pct; Mn, 0.44; P, 0.013; S, 0.033; Si, 0.032. Ingot split at Homestead Works.

In further support of their coincidence, lines *ag*, Fig. 15, correspond closely with the inner lines of inverted-V segregation faintly visible on the left-hand side of the 32x32-in. ingot, Fig. 9.

The Vertical Core: The vertical core of an ingot in a solidification pattern is outlined by the points of tangency between the faces of vertical and transverse solidification, such as point *d'* at 48-in. height in ingot No. 6, Fig. 8b. At the time that transverse solidification is completed at *d'* at 48-in. height, however, vertical solidification has reached a height of only about 45 in. on the vertical axis. Similarly, transverse solidification would be completed at 26-in. height when vertical solidification had reached point *i* in Fig. 14 at 23-in. height on curve *CV* of vertical solidification. Accordingly, point *b'* has been located on extrapolated line bb_e vertically above point *i*. Points *b'* and *d'* have been plotted at their proper depths on both sides of the solidification pattern in Fig. 15. As the width of the vertical core apparently decreases upwardly, so does the differential between the heights of vertical and completed transverse solidification. For this reason, point *g'* has been located on extrapolated line gg_e, Fig. 14, vertically below point *j* at 70-in. height on curve *CV* of vertical solidification. Points *g'* have also been plotted on the solidification pattern in Fig. 15. As the vertical core of an ingot lies directly above the base cone, Fig. 17, the vertical core in the 32x32-in. ingot has been constructed from the tip of the base cone *c* (Fig. 15) through points *b*, *d*, and *g*.

The width of V segregation faintly visible in the upper portion of the split full 32x32-in. ingot, Fig. 9, is approximately equal to the width of the vertical

Fig. 17—Macroetch of 29x66 in. ingot, semikilled steel. Ladle analysis: C, 0.24 pct; Mn, 0.41; P, 0.017; S, 0.036; Si, 0.048. Ingot split at Homestead Works.

core in the corresponding location in the solidification pattern, Fig. 15. This indicates that V segregation is developed in vertical solidification in the vertical cores of ingots.

Isochrones: Isochrones at 20-min intervals have been constructed in the outer zone of the ingot in Fig. 15 parallel to its sides at depths as determined from parabola *OT* in Fig. 14. Curved-line isochrones, spaced on the vertical axis according to the curve of vertical solidification, Fig. 11, have been constructed in the base cone and in the vertical core. The isochrones have been connected by straight lines across the zones of accelerated transverse solidification. Dashed lines $g_e h_e$ correspond in location

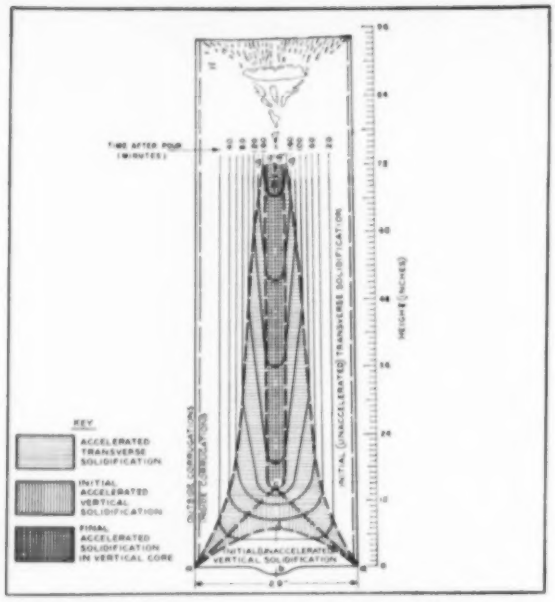


Fig. 18—Solidification pattern of Homestead Works' 29x66 in. big-end-down ingot.

to the actual face of solidification, $g_o h_o$ (Fig. 8b), on the right-hand side of ingot No. 6.

Discussion: With only two points for their establishment, the curves of accelerated transverse solidification, Fig. 14, have been constructed as straight lines. As the spacing of isochrones in the zone of accelerated transverse solidification, Fig. 15, is so nearly uniform, probably little error is involved in this representation.

It is of interest to reconstruct the face of solidification in ingot No. 5, Fig. 8a, from data obtainable from the solidification chart, Fig. 14. As the reconstructed outline $e_5 h_5 e_5$ closely bounds the porous zone, it appears probable that this would be the normal face of solidification.

Solidification Pattern of Big-End-Down Ingots

Although not of the same ingot, the sulphur print (Fig. 16) and macroetch (Fig. 17) of 29x66-in. big-end-down ingots split at Homestead Works appear to match each other closely. The ingots were cast in molds of 9.6-in. mean wall-thickness, having ¾-in. corrugations.

The base cone *aca* and the vertical core *g'cg'*, Fig. 17, of equiaxed crystals are clearly distinguishable by macrostructure. These zones have been outlined on the solidification pattern in Fig. 18. The width of the vertical core, as indicated by two pairs of short lines in the upper portion of the sulphur print, Fig. 16, is about equal to the width of V segregation just above them. This confirms the evidence from the 32x32-in. ingots that V segregation develops in vertical cores of ingots.

Above line *ada* in Fig. 17 vertical columnar crystals slope inwardly, which indicates that transverse components of heat extraction were effective. Zone *adac* in Figs. 17 and 18 is the zone of initial accelerated vertical solidification. As discussed previously, lines *ag* in Figs. 17 and 18, located similarly to inner lines of inverted-V segregation in the sulphur print in Fig. 16, coincide with crystal structure changes, which changes indicate that solidification beyond these lines occurred at accelerated rates. Hence zones *gacg'* in Fig. 18 are zones of accelerated transverse solidification.

Based upon rates of transverse and vertical solidification estimated from the curves in Figs. 12 and 13, respectively, isochrones at 20-min intervals have been constructed in the solidification pattern in Fig. 18.

The solidification pattern of the big-end-down ingot, Fig. 18, and that of the big-end-up ingot, Fig. 15, are similar in that both have a vertical core which extends from the tip of the base cone to the top of the ingot. These vertical cores surmount zones of accelerated vertical solidification and are surrounded by zones of accelerated transverse solidification.

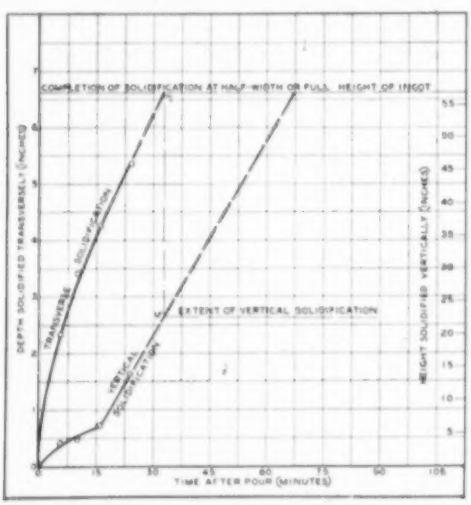

COMPLETION OF SOLIDIFICATION AT HALF-WIDTH OR FULL HEIGHT OF INGOT
DEPTH SOLIDIFIED TRANSVERSELY (INCHES)
HEIGHT SOLIDIFIED VERTICALLY (INCHES)
TRANSVERSE SOLIDIFICATION
VERTICAL SOLIDIFICATION
EXTENT OF VERTICAL SOLIDIFICATION
TIME AFTER POUR (MINUTES)

Fig. 19—Solidification curves for Nelson's 13x13 in. ingot.

Proposed Mechanisms for Segregation in Ingots

Based on the developed solidification patterns of Figs. 15 and 18 and supporting data, the following mechanisms for the several types of segregation in ingots are proposed:

V Segregation: V segregation in ingots appears to result from the entrapment of segregated liquid metal adjacent to the face of vertical solidification by the earlier solidification at higher temperatures of purer metal above the segregated layers. Originally hemispherical, entrapped layers become distorted during cooling, so that they approximate a V shape in ingot sections, Figs. 1, 2, and 3.

In small ingots and in some large ingots of unusual proportions, solidification may be completed transversely rather than vertically. As will be discussed later, the axial characteristics of such ingots differ from those of ingots that develop vertical cores.

Zone of Negative Segregation: Because segregation may ascend readily from the broad face of vertical solidification in the lower portion of an ingot (Figs. 15 and 18), the liquid metal here is relatively pure. Because metal of the highest purity selectively solidifies first,[9] metal of less than average concentration of segregating elements solidifies in the lower middle portions of ingots. As solidification advances upwardly, the concentration of segregation in the liquid and consequently in the solid metal progressively increases, Fig. 1.

Inner Lines of Inverted-V Segregation: The concentration of segregation in the layer of liquid metal

adjacent to the face of transverse solidification increases as solidification rates decrease inwardly. Conversely, when these rates increase, the concentration of segregation must decrease. Thus the excess segregation above that which can be carried at the higher rates is entrapped along the loci of acceleration.

Outer Lines of Inverted-V Segregation: Although outer lines of inverted-V segregation may originate at various heights in an ingot (Fig. 1), all start at approximately the same depth. The beginnings of outer lines of inverted-V segregation have been indicated by the letter x in Homestead Works' 32x32-in. ingots No. 2 (Fig. 6b), 3 and 4 (Fig. 7). According to the theory of selective solidification, there would have been a continuous layer of segregated liquid metal adjacent to the face of solidification in ingot No. 1, Fig. 6a. The presence of termini, x, of segregated layers in ingots Nos. 2, 3, and 4, indicates, therefore, that the originally continuous segregated layer was penetrated at random locations by columnar dendrites. Segregation could rise readily from the upper side, but not from the lower side of a penetrating dendrite. As a segregated layer is slightly insulating,[5] the upper side of the dendrite would then offer a preferred course for heat flow. Hence solidification could advance upwardly beyond the segregated layer and entrap this layer. As solidification progresses upwardly beyond segregated layers, however, transverse solidification continues inwardly. Hence outer lines of inverted-V segregation slope inwardly in an upward direction.

Fragmentary lines of inverted-V segregation, as designated by letters y-y in Fig. 16, sometimes occur inside the prevailing inner lines, ag, of inverted-V segregation, that is, in the zones of accelerated transverse solidification. These segregated layers may be entrapped by a mechanism analogous to that described for the entrapment of outer layers of inverted-V segregation. The increased angles of these lines with the vertical, as compared with those of the prevailing inner lines, ag in Fig. 16, attest to the higher rates of transverse relative to vertical solidification in zones of accelerated transverse solidification as compared with those in outer zones.

Effect of Ingot Design on Solidification Pattern

As the ultimate objective of ingot solidification studies is to improve ingot soundness and uniformity, it seems important to consider the practical aspects of both ingot and mold design.

In the same manner that the curves of transverse and vertical solidification for Homestead Works' 32x32-in. ingot have been plotted on the same chart, Fig. 14, the curves for Nelson's 13x13 and 17x17-in. ingots, respectively, have been plotted together, Figs. 19 and 20. In these two charts also, the vertical scales have been adjusted so that one-half the top width of the ingot on the left-hand scale for transverse solidification equals the full height of the ingot on the right-hand-scale for vertical solidification. The direction in which solidification is completed, then, is determined according to which curve first attains the horizontal line denoting completion of solidification in either direction. As discussed previously, solidification would be completed vertically in the 32x32-in. ingot, Fig. 14. In the 13x13-in. ingot, on the other hand, solidification would be completed transversely, Fig. 19. At the time of this completion, vertical solidification would have attained a relatively short height of only about 22 in.

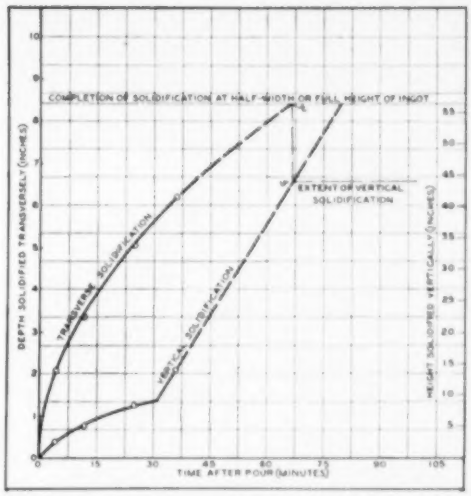

COMPLETION OF SOLIDIFICATION AT HALF-WIDTH OR FULL HEIGHT OF INGOT
TRANSVERSE SOLIDIFICATION
VERTICAL SOLIDIFICATION
EXTENT OF VERTICAL SOLIDIFICATION
DEPTH SOLIDIFIED TRANSVERSELY (INCHES)
HEIGHT SOLIDIFIED VERTICALLY (INCHES)
TIME AFTER POUR (MINUTES)

Fig. 20—Solidification curves for Nelson's 17x17 in. ingot.

In the 17x17-in. ingot, Fig. 20, vertical solidification would have reached a height of about 44 in. at completion of transverse solidification across the top. Hence, in an ingot somewhat shorter than the 17x17-in. ingot, or in one of slightly greater top width, transverse and vertical solidification would be completed to the top middle of the ingot at the same time.

Based upon these three charts, then, it appears that three types of solidification pattern may occur in ingots, Fig. 21. An ingot in which transverse and vertical solidification reach the top middle simultaneously, Fig. 21b, may be termed an ingot of critical w/h ratio. In an ingot of lower than critical w/h ratio, Fig. 21a, vertical solidification does not reach the top of the ingot. The height, v, of the vertical core in ingots of this type decreases with decrease of the w/h ratio. In ingots of greater than critical w/h ratio, Fig. 21c, the width, V_t, of the vertical core at the top increases with increase of w/h ratio.

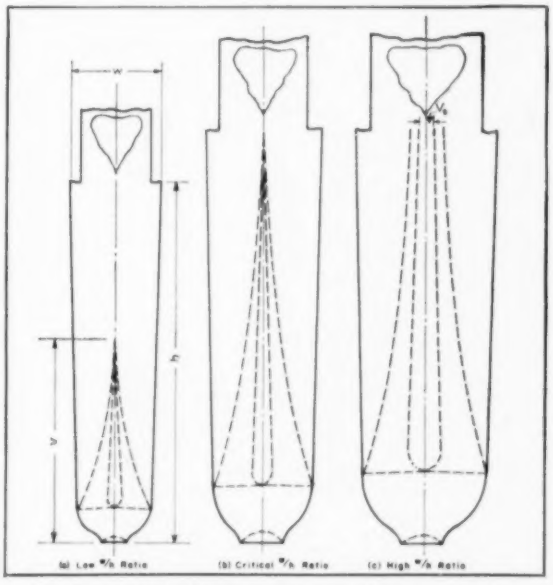


Fig. 21—Typical solidification patterns of ingots of different w/h ratios.

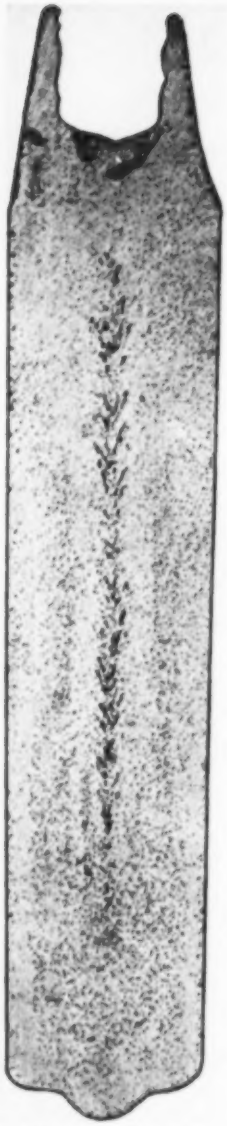


Fig. 22 (above and right)—Sulphur prints of small ingots of low w/h ratio cast in chill and sand molds. Reproduced from the first "Report on the Heterogeneity of Steel Ingots," Iron and Steel Institute, London (1926).

a (above) — Ingot cast in chill mold. Open hearth steel. Ladle analysis: C, 0.50 pct; Mn, 0.83; P, 0.036; S, 0.037; Si, 0.21. Ingot dimensions: 13.8 in. top diameter, 13 in. bottom diameter, 5 ft 5 in. high.

b (right) — Ingot cast in sand mold. Bessemer steel. Ladle analysis: C, 0.48 pct; Mn, 0.82; P, 0.028; S, 0.041; Si, 0.27. Ingot dimensions: 11.9 in. square at top, 10.2 in. square at base, 3 ft 9 in. long.

Fig. 23 (below and right)—Sulphur prints of 26 in. diam ingots of low w/h ratio cast big-end-up and big-end-down in same mold. Ingots split at Homestead Works.

a (below)—Big-end-up. Height of ingot, 164 in. Ladle analysis: C, 0.32 pct; Mn, 0.72; P, 0.035; S, 0.035; Si, 0.26; Ni, 3.37.

b (right)—Big-end-down. Height of ingot, 187 in. Ladle analysis: C, 0.32 pct; Mn, 0.90; P, 0.016; S, 0.022; Si, 0.22; Ni, 2.90.

The top width of an ingot of critical w/h ratio may be termed the critical width for an ingot of given height. The critical width of an ingot will vary with both height and type (big-end-up or big-end-down). From calculations based upon the curves of transverse (Fig. 12) and of vertical (Fig. 13) solidification, the critical width of a big-end-up ingot of 65-in. height is estimated to be about 18 in.; the critical width of a big-end-down ingot of the same height would be somewhat greater, perhaps about 21 in.

The type of solidification pattern, as governed by the w/h ratio, has an important effect on the type and extent of axial defects in ingots. Examples of ingots of all three types are discussed in the following.

Ingots of Low w/h Ratios: Ingots of low w/h ratios are usually comparatively small (say, from 9 to 15 in. sq). Because of their relatively rapid rates of solidification, small ingots develop relatively little segregation. For special applications, however, ingots of much larger sectional areas may be abnormally long, hence have a low w/h ratio.

In Fig. 22a is the sulphur print of a small ingot of low w/h ratio, reproduced from the First Report on the Heterogeneity of Steel Ingots of the British Iron and Steel Institute.[7] The axial characteristics of this ingot are different from those of ingots of higher w/h ratios, Figs. 2 and 3. In the small ingot, the V zone is widest at the top and tapers downwardly to disappearance at about 25 pct above the base. The V-shaped defects are of approximately uniform intensity throughout their extent. The shape of the V zone indicates that the faces of transverse solidification remained parallel to the sides as they advanced inwardly; that is, solidification was completed transversely to the middle of the ingot. Vertical solidification, then, must have been confined to the lower 25 pct of the ingot.

In ingots that complete solidification transversely, the so-called V segregation probably develops according to Hultgren's mechanism[4] described previously; that is, layers of liquid metal are entrapped interdendritically as the faces of solidification from opposite sides meet at the vertical axis. Regardless of the amount of segregation present, porosity develops upon solidification of entrapped liquid metal. For this reason, it appears that V porosity is a more accurate term than V segregation as applied to axial defects in ingots of low w/h ratios.

That V porosity develops also in large ingots of low w/h ratios is apparent from the sulphur print of the 26-in. diam big-end-up ingot split at Homestead Works, Fig. 23a. The large big-end-down ingot of low w/h ratio, Fig. 23b, was cast in the same mold, inverted, as was the big-end-up ingot, Fig. 23a. Because solidification was completed across the top transversely before it was across the lower portion of this ingot, a central cavity developed. Similar cavities will necessarily develop in all big-end-down ingots of low w/h ratio. For big-end-down ingots to be solid, therefore, they must be of high w/h ratio, that is, they must have a vertical core extending to the top of the ingot, Fig. 17.

The wide V's in the ingot of low w/h ratio cast in a sand mold, Fig. 22b, are indicative of a wide core of vertical solidification. Abnormally slow rates of transverse solidification, caused by casting in a sand mold, appear to be responsible for both the abnormally wide vertical core and the abnormally shallow depths of the lines of inverted-V segregation.

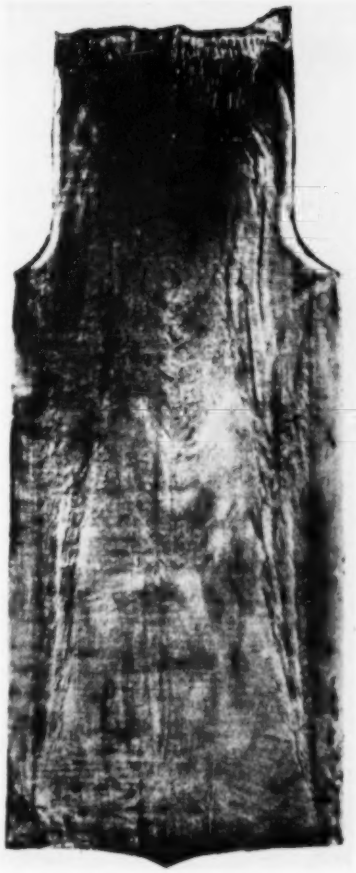


Fig. 24—Sulphur print of 10½ ton big-end-down ingot, electric furnace steel. Ladle analysis: C, 0.30 pct; Mn, 0.74; P, 0.010; S, 0.017; Si, 0.13. Reproduced from first "Report on the Heterogeneity of Steel Ingots," Iron and Steel Institute, London (1926).

Ingots of Near-Critical w/h Ratios: Ingots of near-critical w/h ratios comprise generally those of intermediate sizes, say, from 15 to 25-in. widths. The solidification rates of these ingots are sufficiently slow for a sufficiently long time that appreciable segregation may develop. Since the vertical cores of such ingots are typically narrow (Fig. 21b), segregation may not ascend readily into the sinkhead. For these reasons, V segregation is more prevalent in ingots of near-critical w/h ratios than in ingots of either higher or lower ratios. Big-end-up design effects substantial improvement in the internal soundness of ingots of near-critical w/h ratios, Figs. 2 and 3.

Ingots of High w/h Ratios: Ingots of this type comprise so-called large ingots of over 25-in. width. As the width, V_i in Fig. 21c, of the vertical core at the top increases with increase of the w/h ratio above the critical ratio, ascent of segregates from the liquid metal in the ingot body to the sinkhead is facilitated. Thus, even though large ingots normally develop more segregation than do small ingots, the former, Figs. 4 and 9, may be fully as sound as the latter, Fig. 2.

The width of the vertical core is related to the width of the bottleneck or narrowest space between inner lines of inverted-V segregation in ingots, g-g

Fig. 25 (above)—Sulphur print of large big-end-down ingot. No data supplied. Reproduced from first "Report on the Heterogeneity of Steel Ingots," Iron and Steel Institute, London (1926).

Fig. 26 (right)—Macroetch of 55 in. diam big-end-up ingot. Ladle analysis: C, 0.37 pct; Mn, 0.57; P, 0.018; S, 0.028; Si, 0.19. Ingot split at Homestead Works.

in Figs. 15 and 18. Large ingots, big-end-up as well as big-end-down, in which the bottleneck is too narrow, are subject to excessive V segregation, Fig. 25, and/or secondary pipe, Fig. 26. Large ingots, big-end-down as well as big-end-up, with bottlenecks of adequate width, are typically sound, Figs. 4, 9, and 24.

Mold Design

As discussed above, ascent of segregates into the sinkhead is facilitated by a wide column of liquid metal in the upper portion of an ingot in the final stages of solidification, Figs. 15 and 18. The width of this column is reflected in both the width of the vertical core and that of the bottleneck between inner lines of inverted-V segregation. Differences in these widths constitute the most significant differences between the solidification patterns of big-end-up, Fig. 15, and big-end-down, Fig. 18, ingots. They are reflected in differences in axial soundness between ingots of the two types, Figs. 2 and 3.

Width V_t, Fig. 21c, of the vertical core at the top of an ingot, which may be measured as the width of V segregation, is a convenient single criterion of internal quality. Increased width V_t favors improved ingot soundness. Width V_t is principally dependent upon two factors: 1—the w/h ratio, already discussed, and 2—the relative rates of transverse solidification across the top, and of vertical solidification. Decrease of the former and increase of the latter rates, relative to each other, favor increased width V_t. The relative rates in the two directions may be influenced by the following features of mold design: 1—type of mold, whether big-end-up or big-end-down, 2—mold-wall thickness, and 3—mold-wall taper. The effects of each factor are considered below.

Type of Mold: The advantage of big-end-up design arises principally from the fact that the ingot tops are wider than those of big-end-down ingots; that is, the former ingots have normally higher w/h ratios than the latter. But the narrower, rounded bases of big-end-up ingots favor earlier and more rapid rates of final accelerated vertical

solidification in the vertical cores of these ingots as compared with big-end-down ingots, Figs. 15 and 18. The closed bases of big-end-up molds probably also increase the effectiveness of mold walls in extracting heat. Because their molds are closed-based, big-end-up ingots are sometimes advantageously shorter than big-end-down ingots of similar cross section.

Mold-Wall Thickness: Mold-wall thickness affects the rates of vertical as well as those of transverse solidification. The optimum wall thickness is one that will result in a minimum ratio between rates of transverse and of vertical solidification.

In experiments conducted at Duquesne Works, 25x25-in. ingots cast in molds of 3-in. uniform wall-thickness had narrower *V*,'s and more center segregation than did ingots of the same size cast in molds of standard 5½ in. mean wall-thickness. Apparently the thin wall reduced the rates of vertical solidification relatively more than it did those of transverse solidification. There is evidence, on the other hand, that excessively thick mold walls may increase rates of transverse solidification relatively more than they increase rates of vertical solidification. For example, the mean wall-thickness of the mold in which the 55-in. diam ingot, Fig. 27, was cast was 15⅜ in. The unsound center in the upper portion of this ingot may have been caused by too rapid rates of transverse solidification.

The service life of a mold appears to be related to its wall thickness.[14] Based on studies of extensive data, Bacon[14] finds an optimum M/I ratio (mold weight/ingot weight) of 0.88 for molds of over 6-ton weight. This ratio would result in a 10-in. wall thickness for the above mold.

In summary, for an ingot of any given size there is probably an optimum mold-wall thickness to result in a minimum ratio between rates of transverse and vertical solidification. From superficial scrutiny, it appears probable that optimum mold-wall thicknesses for quality do not vary greatly from those for maximum mold life.

Mold-Wall Taper: Apparently to facilitate solidification from the base upwardly in ingots, mold walls are commonly made 1 to 4 in. thicker at the base than at the top. But dumped ingot data,[1] Fig. 6a, indicate that, except for accelerated solidification, rates of transverse solidification are uniform throughout the height of ingots cast in molds with tapered walls. The reason that mold-wall taper is ineffective for the purpose intended appears to be that heat flows downwardly in mold walls from the thin, hot, top portions to the thick, less hot, base portions. As a result, the normally slower rates of heat extraction by the thin top portions are increased, the normally faster rates of heat extraction by the thick base portions are decreased, and solidification rates are equalized throughout the height of the ingot. Thus, although thick base portions may advantageously increase final rates of accelerated vertical solidification, mold-wall taper appears to be of limited value in improving ingot solidification patterns.

Alloy Steels

The foregoing discussions apply to molds used in casting carbon steels or steels which solidify similarly to carbon steels. Certain low-alloy steels, cast in molds which produce sound carbon-steel ingots, develop exaggerated axial porosity, Fig. 27. Sykes[15] reports "central looseness" in ingots of an austenitic high alloy steel, R. ex 78. Low-alloy steels have

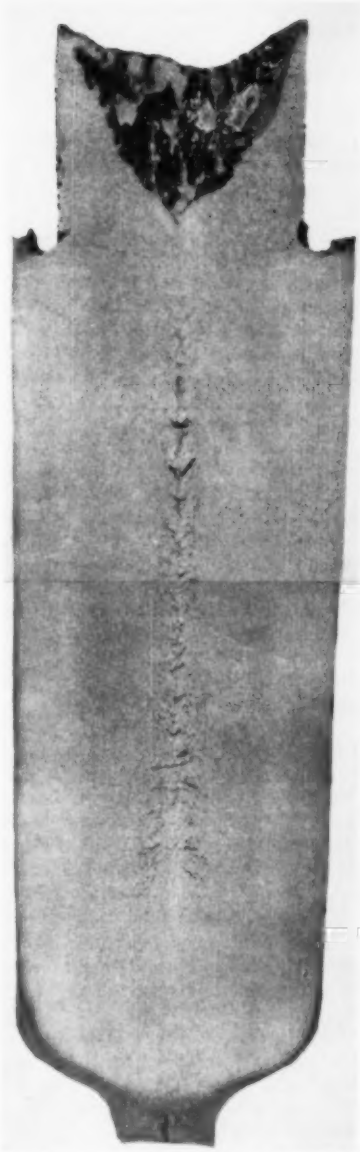


Fig. 27—Macroetch of 22x22 in. ingot, AISI 4340 steel. Ladle analysis: C, 0.40 pct; Mn, 0.68; P, 0.012; S, 0.014; Si, 0.28; Ni, 1.78; Cr, 0.70; Mo, 0.24. Ingot split at Duquesne Works.

strong tendencies toward equiaxed crystals, and austenitic steels toward columnar crystals. Ingots of both types, however, were solid just below the hot-top junction, Fig. 27; that is, solidification was completed transversely across the top before the vertical core was completely solid. Thus the critical w/h ratios, Fig. 21b, for these alloy-steel ingots must be considerably higher than that for carbon-steel ingots.

Sykes determined that exaggerated taper in big-end-up ingots was ineffective in preventing axial porosity. But ingots of R. ex 78 steel cast in sand had completely sound interiors. As shown by the ingot in Fig. 22b, this method of casting results in a wide vertical core. Unfortunately, however, these slow-cooling ingots had excessively large crystals and cracked badly in rolling.

For alloy-steel ingots to be completely sound, it

would be necessary for them to have a higher w/h ratio; that is, to be broader and/or shorter than carbon-steel ingots. From practical considerations, however, the extent to which the w/h ratio may be increased is limited.

Future Trends in Mold Design

As it seems doubtful that w/h ratios of ingots may be increased appreciably above those now used, improved ingot soundness appears to rest upon improved mold design. The benefits to be gained by adjustment of the several factors in molds of conventional design appear to be limited. Although some improvement may be attained by developing the optimum thickness for mold walls, particularly for large molds, there seems to be little prospect for marked gains by adjustment of either ingot or mold-wall taper.

Because of the inherent limitations of molds of conventional design, it seems that departures from conventional mold design should be considered. These should be aimed at increasing rates of vertical solidification and decreasing rates of transverse solidification across the top of an ingot, relative to each other, to the maximum extent practicable. Heat flow in mold walls, which does not appear to have been given adequate attention, needs to be considered.

From viewpoints of both quality and economy, the walls of many large molds in current use appear to be too thick. Further, as large ingots complete solidification vertically rather than transversely, the purpose of excessively thick walls—to reduce the time for complete solidification—is not accomplished. As the advantage of big-end-up over big-end-down casting decreases with increase of ingot size, large ingots may more advantageously be cast in big-end-down molds of moderate wall-thicknesses.

Conclusions

The following conclusions concerning ingot solidification and hypotheses regarding segregation in ingots appear to be consistent with all of the data examined.

In solidifying, ingots develop a core of vertical solidification above the base cone. The vertical core surmounts a zone of accelerated vertical solidification and is surrounded by zones of accelerated transverse solidification.

In ingots of low width/height (w/h) ratio, the vertical core does not reach the top. Above the vertical core, solidification is completed transversely and V porosity may be developed axially.

In ingots of intermediate w/h ratios (15 to 25-in. widths), the vertical core at the top is narrow. Such ingots are subject to excessive V segregation. Big-end-up casting is most advantageously applied to ingots of these ratios.

The width, V_t, of the vertical core at the top of an ingot increases with increase of w/h ratio above the critical ratio. Sound interiors depend upon development of a vertical core of adequate width V_t.

V segregation is formed in the vertical cores of ingots as a result of entrapment of the layer of segregated liquid metal adjacent to the face of vertical solidification by the prior solidification of purer metal above this layer.

The zone of negative segregation in the lower middle portions of ingots develops as a result of selective solidification vertically of the purest metal available from the relatively pure metal in the lower portion of the contained liquid metal.

Inner layers or lines of inverted-V segregation result from the entrapment of excess segregation above that which can be carried forward at accelerated rates of transverse solidification. Outer layers or lines of inverted-V segregation result from penetration of the segregated layer of liquid metal adjacent to the face of solidification by columnar dendrites. Following such penetration, solidification may progress inwardly and upwardly, and entrap the segregated layer.

Little improvement in internal quality of ingots may be anticipated from increase of ingot taper or mold-wall taper beyond those now used in molds of current design.

There appears to be an optimum mold-wall thickness for each ingot size to result in maximum width of vertical core, V_t, at the top of an ingot. The walls of some molds of current design, particularly those for large ingots, appear to be too heavy from both quality and economy viewpoints.

Departures from current mold design should be considered. These should be aimed at increasing rates of vertical relative to those of transverse solidification in ingots.

Acknowledgments

The interest and cooperation of staff members of the Metallurgical Dept., Homestead Works, in these ingot solidification studies, particularly their permission to use the photographs of the split dumped 32x32-in. ingots and other ingots, is acknowledged. It is desired also to express appreciation of the considerable amount of experimental work performed by the Metallurgical Dept., Duquesne Works, some of which has been mentioned. Thanks are extended to the several members of the staff of the Research and Development Division for their constructive suggestions and criticism in the preparation of this paper.

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Aluminum-Oxygen Equilibrium in Liquid Iron

by Nev A. Gokcen and John Chipman

Aluminum and oxygen dissolved in liquid iron were brought into equilibrium with pure alumina crucibles and atmospheres of known H_2O and H_2 contents to study the reactions: 1—$Al_2O_3(s) = 2\,Al + 3\,O$; 2—$Al_2O_3(s) + 3H_2(g) = 2\,Al + 3H_2O(g)$; and 3—$H_2(g) + O = H_2O(g)$. Aluminum strongly reduces the activity coefficient of oxygen and similarly oxygen reduces that of aluminum. Values of the product $[\%\ Al]^2 \cdot [\%\ O]^3$ are much smaller than those found in previous experimental studies and are of the order of magnitude of the calculated values.

ALUMINUM is the strongest deoxidizer commonly used in steelmaking, but the extent to which it removes dissolved oxygen has been debatable. The relationship between aluminum and oxygen has not been determined reliably not only on account of the usual experimental difficulties at high temperatures but also because of uncertainties in the analyses of very small concentrations of oxygen and aluminum.

The earliest experimental attempt of Herty and coworkers[1] was followed by a more systematic study of Wentrup and Hieber.[2] These authors added aluminum to liquid iron of high oxygen content in an induction furnace and considered that 10 min was sufficient to remove the deoxidation products from the melt. Parts of the melts thus obtained were poured into a copper mold and analyzed for total aluminum and oxygen (soluble plus insoluble forms), assuming that the insoluble parts were in solution at the temperatures from which samples were taken. It is conceivable that the furnace atmosphere in their experiments, consisting of mainly air at 20 mm Hg pressure, was a serious source of continuous oxidation and therefore that their oxygen concentrations were correspondingly high. Scattering of their data was explained to be well within the maximum inaccuracy of 10°C in the temperature measurements and errors of ±0.002 pct each in the oxygen and total aluminum analyses. Maximum and minimum deoxidation values, i.e., values of the product $[\%\ Al]^2 \cdot [\%\ O]^3$ differed by factors of 10 to 15; mean values of 9×10^{-11} and 7.5×10^{-9} were reported at 1600° and 1700°C, respectively.

Hilty and Crafts[3] determined the solubility of oxygen in liquid iron containing aluminum, using a rotating induction furnace. Pure alumina crucibles used in their experiments contained the liquid iron which in turn acted as a container for slags of varying compositions consisting mainly of Al_2O_3, Fe_2O_3, and FeO. The furnace was continuously flushed with argon, and additions of aluminum and Fe_2O_3 were made in the course of each experimental heat. The inner surfaces of their alumina crucibles were covered with a substance other than pure Al_2O_3, containing both iron oxide and alumina. Although frequent slag additions can change the composition of slag in the liquid iron cup formed by rotation, the inner surface of the crucible must depend upon the transfer of oxygen or aluminum through the liquid iron for any adjustment in composition. It is not clear that their metal was in equilibrium with the crucible wall, but it is clear that it was not in equilibrium with Al_2O_3. Their deoxidation product, $[\%\ Al]^2 \cdot [\%\ O]^3$, varied by a factor of more than 50; the average values of 2.8×10^{-9} and 1.0×10^{-7} were selected for temperatures of 1600° and 1700°C, respectively.

Aside from the experimental determinations, attempts have been made to calculate the deoxidation constant for aluminum indirectly from thermodynamic data. Schenck[4] combined the thermodynamic data for Al_2O_3 and dissolved oxygen in liquid iron by assuming an ideal solution. His calculated values are 2.0×10^{-15} and 3.2×10^{-13} at 1600° and 1700°C, respectively. Later, Chipman[5] attempted to correct for the deviation from ideality and derived an expression which led to deoxidation values of 2.0×10^{-14} and 1.1×10^{-12} at 1600° and 1700°C, respectively. The errors in these treatments originate mainly from inaccuracies of thermal data and uncertainties regarding the activity coefficients of dissolved oxygen and aluminum.

The purpose of this investigation was to study the equilibria represented in the following reactions in the presence of pure alumina:

$$Al_2O_3(s) = 2\underline{Al} + 3\underline{O} \qquad K_1 = a_{Al}^2 \cdot a_O^3 \qquad [1]$$

$$Al_2O_3(s) + 3H_2(g) = 2\underline{Al} + 3H_2O(g) \qquad K_2 = a_{Al}^2 \left(\frac{H_2O}{H_2}\right)^3 \qquad [2]$$

$$H_2(g) + \underline{O} = H_2O(g) \qquad K_3 = \frac{1}{a_O}\left(\frac{H_2O}{H_2}\right) \qquad [3]$$

The experimental method consisted of melting pure electrolytic iron, usually with an initial charge of aluminum, in pure dense alumina crucibles under a controlled atmosphere of H_2O and H_2 and holding

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Table I. Approach to Equilibrium

Heat No.	Hours at Temperature	Al, Pct		O, Pct
		Charge	Analyzed	
205*	5.77	0.00	0.0094	0.0035
204*	10.25	0.00	0.0105	0.0040
207	1.0	0.00	0.011	0.0058
206	3.0	0.00	0.0126	0.0056
208	6.7	0.00	0.018	0.0041
209	2.17	0.017	0.015	0.0052
210	4.17	0.032	0.014	0.0050
211	5.1	0.047	0.015	0.0048
212	5.1	0.060	0.026	0.0053

* Heats 204 and 205 were made at 1680°C and $H_2O/H_2 = 5.12 \times 10^{-3}$. Others were made at 1723°C and $H_2O/H_2 = 3.72 \times 10^{-3}$.

it at a constant temperature until equilibrium was established between gas, liquid, and solid phases. The resulting melts of very small weight were quenched to retain the equilibrium concentrations of aluminum and oxygen and subsequently analyzed for these elements. The apparatus and procedure followed herein were described earlier in detail.[6]

In order to obtain concentrations of aluminum and oxygen high enough for analysis, it was planned to operate at temperatures higher than those used in previous studies.

Experimental Procedure

The procedure employed in these experiments was quite similar to that employed in the previous investigation.[6] The main differences were as follows:

Slightly lower preheater temperatures were used in order to conserve the heating coil inside preheater. This was necessitated by the relatively dry hydrogen employed which had a strong tendency to embrittle the Pt-Rh alloy.

Experiments were conducted at considerably higher temperatures in order to obtain sufficient amounts of aluminum and oxygen for dependable analysis. At the usual experimental temperature of 1600°C, either the aluminum or the oxygen was always too low for accurate determination.

The temperature control and the accuracy of its measurement were within ±10°C even at the highest temperature used, 1866°C.

Known mixtures of H_2O and H_2 were obtained by passing purified hydrogen through the saturated solution of lithium chloride at various controlled temperatures. The vapor pressure of this solution had been determined previously in the same apparatus.[7] The saturated hydrogen was mixed with four times its volume of purified argon.

Alumina crucibles used in this work were of the highest purity with less than 2 pct porosity. They were 1 in. high and 1 in. OD with a wall thickness of 0.04 in.

Operation: The charge consisted of 32 g of electrolytic iron containing a small percentage of aluminum in the form of pure Fe-Al alloy. The crucible was inserted in the furnace to the point where the surface of metal was 0.2 in. below the preheater. The preheater was brought to the desired temperature and the furnace flushed for a minimum period of 2 hr. Then the induction unit was turned on and the charge was brought to the desired temperature of 1700°C or more in less than 80 sec in order to preserve the aluminum in the charge. If the charge contained aluminum far beyond the equilibrium concentration, a thin and persistent scum of Al_2O_3 was formed on its surface a short time after reaching the desired temperature. Such heats were rejected, and a very thin grayish white solid scum was observed on the quenched melts. In the satisfactorily charged heats the surface of melt was uniform and clean, permitting accurate temperature measurements with an optical pyrometer. After the attainment of equilibrium, the melts were quenched with hydrogen as described in the following section. Quenched equilibrium melts were shiny on the top and loosely attached to the alumina crucibles. Crucibles were only slightly discolored at 1866°C and were white at lower temperatures.

Quenching: The crucible was lowered into a position between two groups of orifices through which jets of hydrogen were directed upon it. Dense and very thin alumina crucibles without any radiation shields were used to facilitate the quenching process. It was found that by lowering the crucible into the cold zone of the silica furnace tube without the hydrogen jet the melt required a period of 60 sec to freeze, whereas in hydrogen quenching 7 to 12 sec was sufficient depending upon the temperature of melts.

Occasionally melts were spilled on the brass bottom when the crucibles cracked due to severe thermal shocks, thereby yielding severely quenched sound samples.

Oxygen Analysis: Oxygen analyses were made by the vacuum-fusion technique in the usual manner. The following precautions were taken to minimize the errors in the analytical results: Larger samples of 5 to 8 g were used. Very low and consistent blanks were obtained before proceeding with the analysis. This was accomplished by a long period of degassing of the vacuum-fusion apparatus. The aluminum content of the melt in the vacuum-fusion crucible was kept below 0.03 pct. Independent analyses were made by N. A. Gokcen to check the accuracy in the results.

The reproducibility of the oxygen analyses was generally within ±0.0005 pct O.

Aluminum Analysis: Determination of aluminum was made by the gravimetric method[8] in the range of 0.010 to 0.06 pct Al. The colorimetric method of analysis using aluminon as the indicator was used throughout the range investigated, yielding the soluble and insoluble aluminum separately. The agreement between the two methods was usually less than 0.001 pct in aluminum. The insoluble aluminum was approximately constant at each temperature, the average values being 0.0025, 0.0030, and 0.0055 at 1695°, 1760°, and 1866°C, respectively. In the absence of insoluble analyses for a very few heats, the average at each temperature level was added to the soluble aluminum content to obtain the total concentration. Average deviation in the duplicate analyses of total aluminum was always below ±0.001 pct Al and usually of the order of ±0.0006 pct.

Experimental Results

Attainment of Equilibrium: The experimental heats in Table I were made in order to ascertain the approximate time required for the establishment of equilibrium between three phases: gas, liquid metal, and solid alumina. Heats 294 and 205 were made at 1680°C under identical atmospheres without any aluminum in the charge. Analysis indicated that most of the aluminum was picked up from the crucible in about 6 hr, but there is no certainty that equilibrium was reached in 10 hr. Heat 208, with no aluminum in the charge, reached a slightly higher concentration than the next three in which the charge was above the final value. These four heats

must be regarded as having reached equilibrium within the limitations of the method.

Aluminum several times higher than the equilibrium value resulted in the formation of a thin and persistent scum of alumina covering the entire surface of liquid iron.

Heats 209, 210, and 211 indicate that by charging aluminum the time required for the attainment of equilibrium was reduced. Generally, heats were charged with an amount of aluminum slightly higher than the expected equilibrium concentration, and a period of time usually exceeding 8 hr was employed to reach equilibrium. Further increase in time was unjustified since the analysis for aluminum is not sufficiently precise to indicate small deviations from equilibrium.

Equilibrium Data: Table II gives the complete data on 20 equilibrium heats at 1695°, 1760°, and 1866°C. Tabulated also are values of the "apparent equilibrium constants" corresponding to Eqs. 1, 2, and 3, namely:

$$K_1' = [\%\ \mathrm{Al}]^2\,[\%\ \mathrm{O}]^3$$

$$K_2' = [\%\ \mathrm{Al}]^2 \left(\frac{\mathrm{H_2O}}{\mathrm{H_2}}\right)^3$$

$$K_3' = \frac{1}{[\%\ \mathrm{O}]} \left(\frac{\mathrm{H_2O}}{\mathrm{H_2}}\right)$$

Thermodynamic Calculations

Oxygen: The equilibrium represented by Eq. 3 has been studied, at higher oxygen levels, by Dastur and Chipman.[8] Theoretically, the activity coefficient of oxygen in each of the melts reported here is easily found by dividing the value of K_3' by their value of K_3. This procedure, however, leads to extremely low values for the activity coefficient, so low, in fact, that the present authors are reluctant to put them forward. It seems possible that the results reported here, which are all at very low oxygen concentrations, may contain some small systematic error which makes these values of K_3' a little lower than they should be. In view of this possibility, no attempt will be made to correlate them with Dastur's data.

In Fig. 1 observed values of log K_3' at the two highest temperatures are plotted against the percentage of aluminum. Dastur's points are plotted at zero aluminum but are ignored in drawing the lines.

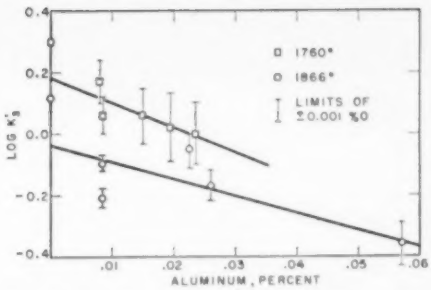

Fig. 1—Experimental values of log K_3' or log $(H_2O)/(H_2)[\%O]$. Limits indicate effect of error of ±0.001 pct in analysis for oxygen.

The effect of an error of ± 0.001 pct in oxygen analysis is indicated to emphasize the sensitivity of the plot. Actual deviations should be ascribed as much to errors in gas composition as to oxygen analysis. Since the experimental values of log K_3' are not constant it is evident that the activity coefficient of oxygen varies with the concentration of aluminum. Previous work has shown that in the binary system Fe-O the activity coefficient is constant; hence, variations in the ternary system may be ascribed entirely to the effect of the third component. The slopes of the lines in Fig. 1 represent values of the coefficient $\partial \log f_o / \partial [\%\ \mathrm{Al}]$ which shall be designated here by the symbol $e_o^{(Al)}$. Since log f_o is zero in the absence of aluminum it follows that within the range of concentrations in which $e_o^{(Al)}$ is constant:

$$\log f_o = e_o^{(Al)}\,[\%\ \mathrm{Al}] \qquad [4]$$

The slopes of the two lines of Fig. 1 yield values of $e_o^{(Al)} = -5.6$ and -8.0 at 1866° and 1760°, respectively; the data for 1695° agree roughly with those for 1760°. It is evident that the data do not yield accurate values of this quantity but that the figures given are conservative, for if the lines had been drawn to Dastur's points, the numbers would have been about doubled. The uncertainty is regrettable but is inherent in the very low concentrations involved.

Table II. Equilibrium Data at 1695°, 1760°, and 1866°C

Heat No.	Al, Pct Charged	Al, Pct Analyzed	$H_2O/H_2 \times 10^5$ Corrected	Hours at Temperature	O, Pct	K_2'	K_3'	K_1'
At 1695°C:								
235	0.021	0.0038	9.63	7.5	0.0065*	12.9×10^{-12}	1.48	3.94×10^{-12}
233	0.030	0.0045	7.04	7.5	0.0052	7.03×10^{-12}	1.35	2.84×10^{-12}
234	0.033	0.0073†	5.18	10.7	0.0038	7.48×10^{-12}	1.36	2.92×10^{-12}
226	0.045	0.0125	3.75	11.4	0.0032*	5.27×10^{-12}	1.17	5.11×10^{-12}
221	0.049	0.0164	2.32	12.8	0.0026	3.37×10^{-12}	0.89	4.73×10^{-12}
220	0.051	0.0230	1.95	13.0	—	3.92×10^{-12}	—	—
At 1760°C:								
225	0.027	0.0050	13.03	13.8	—	5.52×10^{-11}	—	—
224	0.032	0.0080	9.58	12.1	0.0065	5.62×10^{-11}	1.47	1.76×10^{-11}
231	0.029	—	7.02	8.0	0.0075	—	0.94	—
232	0.000	0.0080	7.04	8.0	0.0062	2.24×10^{-11}	1.14	1.52×10^{-11}
218	0.042	0.0150	5.25	9.0	0.0046	3.26×10^{-11}	1.14	2.19×10^{-11}
217	0.042	0.023	3.80	8.7	0.0038	2.90×10^{-11}	1.00	2.90×10^{-11}
223	0.056	0.0190†	3.78	10.5	0.0036	1.95×10^{-11}	1.05	1.62×10^{-11}
At 1866°C:								
230	0.028	0.0085†	13.03	7.7	0.0164	1.59×10^{-10}	0.80	3.19×10^{-10}
229	0.026	0.0086†	9.59	8.0	0.0155	0.65×10^{-10}	0.62	2.75×10^{-10}
216	0.041	0.0230	7.12	6.1	0.0080	1.91×10^{-10}	0.89	2.70×10^{-10}
228	0.042	0.0335	5.24	6.6	—	1.62×10^{-10}	—	—
227	0.049	0.0260†	5.19	9.8	0.0076	0.95×10^{-10}	0.68	2.97×10^{-10}
215	0.047	0.044	3.50	5.7	—	—	—	—
214	0.061	0.0570	2.45	6.0	0.0057*	0.48×10^{-10}	0.43	6.00×10^{-10}

* Single analysis.
† Average deviation about 0.0010; in all other cases, less than 0.0006.

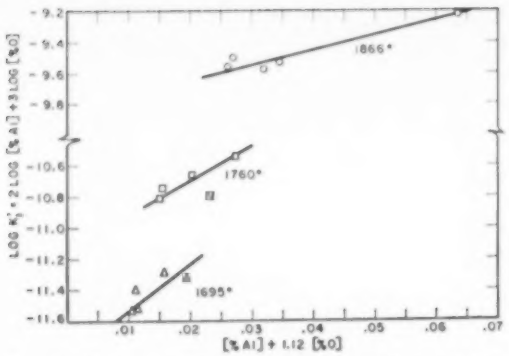

Fig. 2—Effect of concentration on equilibrium product $[\%\ Al]^2\,[\%\ O]^3$.

Interaction of Al and O: The attractive forces between dissolved atoms of aluminum and oxygen which give rise to the effect discussed above also lead to variation in values of the equilibrium product $[\%\ Al]^2\,[\%\ O]^3$. Before examining the data on this product it will be helpful to review briefly the thermodynamics of ternary solutions which are very dilute with respect to two components.

For the limiting case of a solution which is infinitely dilute with respect to components 2 and 3 in the solvent 1, Wagner[9] has introduced the coefficients

$$\epsilon_2^{(2)} = \partial \ln f_2 / \partial N_2 \qquad [5]$$

$$\epsilon_2^{(3)} = \partial \ln f_2 / \partial N_3, \text{ etc.}$$

and has shown that

$$\epsilon_2^{(3)} = \epsilon_3^{(2)} \qquad [6]$$

In the very dilute solutions which are the concern here, it is reasonable to assume that Eq. 6 remains valid and further that $\epsilon_{Al}^{(Al)}$ and $\epsilon_O^{(O)}$ are negligible. Variations in the activity coefficient of oxygen are ascribed entirely to the effect of aluminum and, reciprocally, variations in f_{Al} are regarded as effects of oxygen. The quantity $\epsilon_O^{(Al)}$ or $\epsilon_{Al}^{(O)}$ may be regarded as an interaction parameter which most conveniently represents the effect of one element on the thermodynamic behavior of the other. The parameter is expected to vary with temperature, but at constant temperature the value determined at infinite dilution may remain constant over a considerable range of concentration.

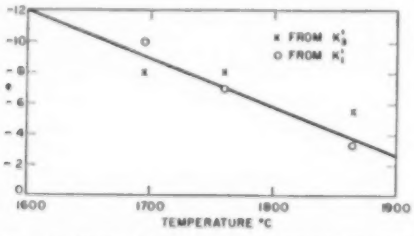

Fig. 3—Effect of temperature on interaction parameter $e_O^{(Al)} = \partial \log f_O / \partial [\%\ Al]$.

The coefficient $e_O^{(Al)}$ used in the preceding section is related to $\epsilon_O^{(Al)}$ in the manner that atom fraction is related to weight percent. Introduction of the necessary numbers reduces Eq. 6 to the following form which is valid within the composition range in which the e's are constant:

$$e_{Al}^{(O)} = \log f_{Al} / [\%\ O] = \frac{27}{16} e_O^{(Al)} \qquad [7]$$

The equilibrium constant for the deoxidation reaction, Eq 1, may be expressed as follows:

$$K_1 = [\%\ Al]^2 \cdot [\%\ O]^3 \cdot f_{Al}^2 \cdot f_O^3$$

$$\log K_1 = \log K_1' + 2 \log f_{Al} + 3 \log f_O$$

$$= \log K_1' + 2 e_{Al}^{(O)} [\%\ O] + 3 e_O^{(Al)} [\%\ Al] \qquad [8]$$

which, in view of Eq. 7, becomes

$$\log K_1 = \log K_1' + 3.37\, e_O^{(Al)} [\%\ O] + 3\, e_O^{(Al)} [\%\ Al]$$

$$= \log K_1' + 3\, e_O^{(Al)} (1.12\, [\%\ O] + [\%\ Al]) \qquad [9]$$

In Fig. 2 the experimental values of log K_1' are plotted against $(1.12\ [\%\ O] + [\%\ Al])$. The slope of the line represents $3e_O^{(Al)}$ at each temperature. The intercept would represent log K_1 but a more representative value will be found after establishing average values of $e_O^{(Al)}$ and $e_{Al}^{(O)}$. The slopes of the three lines correspond to values of $e_O^{(Al)}$ of −3.3, −7, and −10 at 1866°, 1760°, and 1695°, respectively.

The two sets of values of $e_O^{(Al)}$ are plotted against temperature in Fig. 3. These are not entirely independent sets since both involve oxygen analyses. The first set derived from Fig. 1 depends upon gas composition, the second does not. An average line is extrapolated to 1600° and the best values of the coefficients at several temperatures are assembled in Table III.

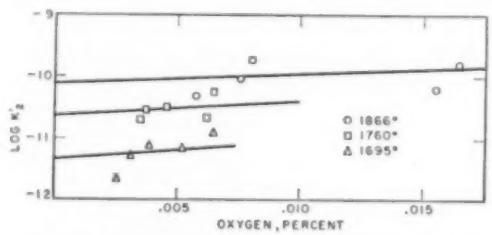

Fig. 4—Experimental values of log K_2' or log $[\%\ Al]^2 (H_2O)^3/(H_2)^3$.

It is interesting to compare the effects of aluminum on the activity coefficient with those of other elements that have been studied.[10] Both chromium and vanadium diminish the activity coefficient of oxygen and are trivalent, like aluminum, and hence comparable. The order of arrangement of the three is the same as that of the heats of formation of the oxides. Table IV shows the comparison. In a very general way, the effect on the activity coefficient parallels deoxidizing power of the three elements as represented by the free energy change in reactions of the type of Eq. 3. The tabulated values are taken from ref. 10.

Aluminum in Iron: The effect of oxygen on the activity of aluminum has been shown in Table III. The corresponding effect on log K_2' is shown in Fig. 4 in which the lines are drawn with the slopes required by Table III. It is evident that the data do not afford accurate estimates of these slopes but that

Table III. Interaction Parameters of Aluminum and Oxygen in Liquid Iron

Temperature °C	1600	1695	1760	1866
$e_O^{(Al)} = \partial \log f_O / \partial [\%\ Al]$	−12	−9	−7.0	−3.6
$e_{Al}^{(O)} = \partial \log f_{Al} / \partial [\%\ O]$	−20	−15	−12	−6.0
$\epsilon = \partial \ln f_O / \partial N_{Al}$	−1340	−1000	−780	−400

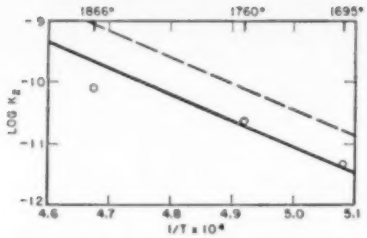

Fig. 5—Effect of temperature on log K_2'. Dotted line calculated from ref. 10. Solid line best average.

again the effect is estimated conservatively since greater slopes would fit the data equally well.

The limiting values of log K_2' at zero oxygen represent log K_2 at the three temperatures. It is obvious that these are subject to uncertainties of ± 0.5 or greater. Nevertheless, they are of interest as the only experimental values of this equilibrium constant. In Fig. 5 they are plotted against the reciprocal of absolute temperatures and compared with the calculated values of ref. 10. The calculated slope is probably better than could be obtained from the present data and this is used to draw the solid line whose equation is

$$\log K_2 = -42850/T + 10.37 \qquad [10]$$

Eq. 10 deviates from the data of ref. 10 by about 0.6 in log K_2. If this is attributed entirely to deviation in the gas composition, it is equivalent to 0.2 in the logarithm of the ratio $(H_2O)/H_2$, the values of this investigation being low by that amount. Similarly in Fig. 1 the deviations in log K_2' correspond to ratios that are low to the extent of 0.12 to 0.16 in log K_2 at 1760° and 1866°, respectively. It is not possible at the present time to assign causes of this deviation nor to be sure that it resides in the gas composition.

Deoxidation Constant: Returning to Eq. 1, the equilibrium constant for the deoxidation reaction is calculated in Table V. This includes data on two heats in Table I which appear to have reached equilibrium as well as those in Table II. The average values of log K_1 at each temperature are plotted in Fig. 6. The straight line, which represents the calculated line given in ref. 11, is fitted by the equation

$$K_1 = a_{Al}^2 \cdot a_O^3; \log K_1 = -64000/T + 20.48 \qquad [11]$$

The agreement is surprisingly good. Although the new data indicate a slightly smaller temperature coefficient, they are not sufficiently accurate to warrant a change and the equation of ref. 11 is considered satisfactory as it stands. It must be noted that the equation applies to activities rather than percentage concentrations.

Table IV. Comparison of the Effects of Three Elements on Activity Coefficient of Oxygen at 1600°

	Chromium	Vanadium	Aluminum
$e_O^{(x)} = \partial \log f_O/\partial [\% X]$	—0.06	—0.25	—12
$\epsilon = \partial \ln f_O/\partial N_x$	—13	—53	—1340
ΔH for formation of X_2O_3, kcal at 25°C	—269	—296	—399
$\Delta F°$ for reaction $2X + 3O = X_2O_3$ kcal at 1600°C	—32	—50	—117

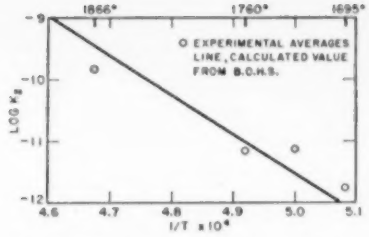

Fig. 6—Effect of temperature on the deoxidation constant, $a_{Al}^2 \times a_O^3$.

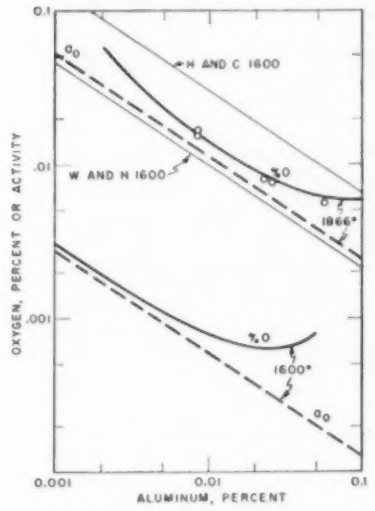

Fig. 7—Comparison of data on aluminum deoxidation. Broken lines show oxygen activities at 1600° and 1866°. Curved solid lines are corresponding percentages. Experimental points at 1866° are shown. Data of Hilty and Crafts and of Wentrup and Hieber at 1600° are shown.

For comparison with other data on aluminum deoxidation, Eq. 11 is used to obtain an extrapolated value of K_1 at 1600° of 2×10^{-14}. This is thought to be a more reliable figure than could have been obtained by a direct experimental approach using our method. To obtain corresponding values for actual concentrations of aluminum and oxygen requires use of the extrapolated interaction parameters of

Table V. Calculation of Equilibrium Constant $K_1 = a_{Al}^2 \cdot a_O^3$

Temperature	Heat No.	Log K_1'	3 Log f_O	2 Log f_{Al}	Log K_1
1680°	204	—11.15	—0.30	—0.13	—11.58
1695°	235	—11.41	—0.10	—0.19	—11.70
	233	—11.55	—0.12	—0.15	—11.82
	234	—11.54	—0.20	—0.11	—11.85
	226	—11.29	—0.34	—0.10	—11.73
	221	—11.32	—0.44	—0.08	—11.84
				Average	—11.78
1723°	208	—10.64	—0.43	—0.11	—11.18
	210	—10.60	—0.34	—0.14	—11.08
				Average	—11.13
1760°	224	—10.75	—0.18	—0.16	—11.19
	232	—10.82	—0.18	—0.15	—11.15
	218	—10.66	—0.34	—0.11	—11.11
	217	—10.54	—0.52	—0.09	—11.15
	223	—10.79	—0.43	—0.09	—11.31
				Average	—11.18
1866°	230	—9.50	—0.07	—0.19	—9.76
	229	—9.56	—0.07	—0.18	—9.81
	216	—9.57	—0.24	—0.09	—9.90
	227	—9.53	—0.27	—0.08	—9.88
	214	—9.22	—0.60	—0.07	—9.89
				Average	—9.85

Table III together with Eq. 9. The results of this calculation are shown in Fig. 7 along with the experimental data for 1866°C. Experimental results of Wentrup and Hieber[2] and of Hilty and Crafts[3] at 1600° are included. No attempt will be made here to account for the discrepancy.[10] The low activity coefficients provide only a small correction.

Summary

An experimental study has been made on the equilibrium of liquid iron containing aluminum and oxygen with a gaseous mixture of hydrogen and water vapor and with crucibles of pure Al_2O_3 at temperatures in the range 1695° to 1866°C. The results were used to obtain activity coefficients of aluminum and oxygen in the solution and the equilibrium constants of the several reactions.

The activity of oxygen is strongly reduced by the presence of aluminum and reciprocally oxygen reduces that of aluminum. The effect diminishes with increasing temperature.

Equilibrium constants are in approximate agreement with calculations based on data of "Basic Open Hearth Steelmaking." The "deoxidation constant," $a_{Al}^2 \cdot a_O^3$ is represented by the equation

$$\log K_1 = -64000/T + 20.48$$

The experimental values of the product $[\%\ Al]^2 \cdot [\%\ O]^3$ are much lower than results of Wentrup and Hieber or of Hilty and Crafts. The discrepancy is not accounted for by the low activity coefficients.

Acknowledgment

This work was sponsored by the Office of Naval Research under Contract No. N5 ori-78/XVI.

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Technical Note

Low Temperature Aging in Titanium Alloys

by W. M. Parris, L. L. Hirsch, and P. D. Frost

IT has been established that titanium alloys containing sufficient amounts of β-stabilizing elements, such as iron, chromium, or manganese, can be age hardened.[1] Adenstedt, Pequignot, and Raymer[2] showed that age hardening occurred in a Ti-15 pct V alloy at room temperature after it was quenched from a temperature in the β-phase region.

During a recent investigation of the heat-treating characteristics of binary Ti-Mn and Ti-Cr alloys at Battelle, further evidence of low temperature aging was found. Appreciable hardening occurred in some of these alloys at aging temperatures as low as 212°F (100°C). Indeed, the brief heating period employed for mounting metallographic specimens in bakelite resulted in hardening. It was felt that further information on this low temperature aging phenomenon would be of general interest in view of the large amount of work currently being done on titanium alloys.

The alloys examined in this investigation were arc-melted in a water-cooled copper crucible as ¾-lb ingots. Du Pont Process A sponge was used as a base material. The arc-melted ingots were forged at 1700° to 1800°F (927° to 982°C) and hot rolled at 1450°F (788°C) to 14 gage (0.064 in.) sheet. Small specimens were heated in argon at 1742°F (950°C) for 30 min and quenched in various liquid media or air cooled. They were then mounted in a room-temperature-setting resin and given a metallographic

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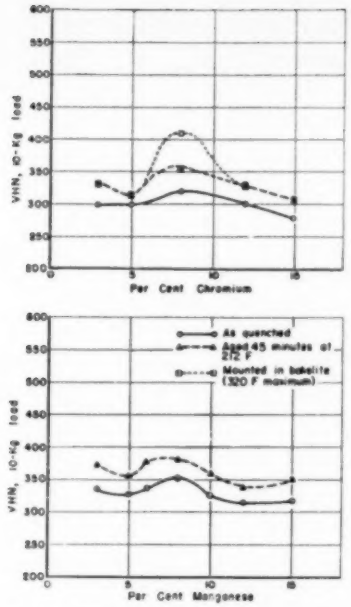

Fig. 1—Effects of low temperature reheating on titanium alloy specimens quenched in ice water from 1742°F (950°C).

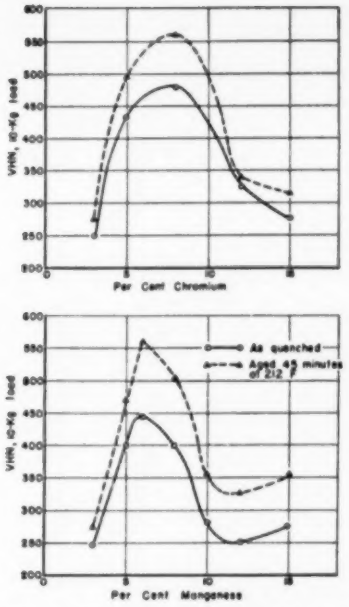

Fig. 3—Effects of low temperature reheating on titanium alloy specimens air cooled from 1742°F (950°C).

polish. After Vickers hardness determinations had been made on these specimens, they were heated in boiling water (212°F) for 45 min and again subjected to hardness tests. Results of these tests are plotted in Figs. 1 to 3. (Each point in the curves represents the average of at least three hardness determinations.) Also included in Figs. 1 and 2 are curves representing the effect of mounting in bakelite on the hardness of the series of Ti-Cr specimens. The maximum temperature attained during the curing of the bakelite mounts was 320°F (160°C). Upon attaining this temperature, the mounts were rapidly cooled to room temperature.

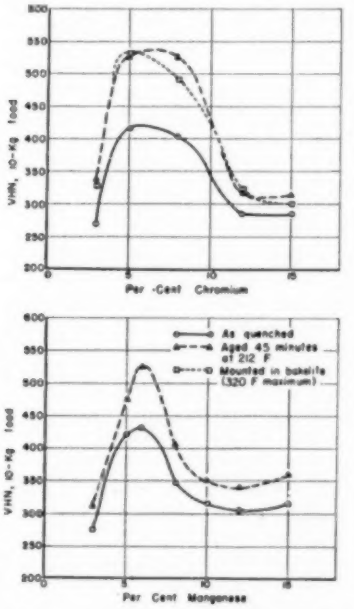

Fig. 2—Effects of low temperature reheating on titanium alloy specimens quenched in liquid nitrogen from 1742°F (950°C).

It is evident that some hardening occurred in all of the alloys under all conditions of prior heat treatment when they were reheated to 212°F. Hardness increases in the water-quenched specimens were moderate, averaging about 25 VHN. However, specimens cooled at the lower rates (liquid-nitrogen quench or air cooled) exhibited hardness increases of over 100 VHN in some cases. The alloys which contain 5 and 8 pct Cr, or 5, 6, and 8 pct Mn, hardened considerably more than those of lower or higher alloy contents. With the exception of the water-quenched 8 pct Cr alloy, the hardnesses of the bakelite-mounted specimens agreed very well with those of the specimens aged at 212°F.

This work demonstrates that it is possible to introduce large increases in hardness in certain titanium alloys by heating in the range 200° to 300°F. The effects of variation in aging time and temperature on the hardness and other properties of the alloys described have not been fully investigated. Likewise, the study has been applied to relatively few alloys. The aging phenomenon warrants further investigation. It will certainly be of interest to those who have been using bakelite mounts for examining the microstructures of titanium alloys. However, it may be of greater future significance in processing alloys for structural applications.

The information in this note was obtained in research on titanium alloys being conducted at Battelle Memorial Institute for the Materials Laboratory of the Wright Air Development Center, Contract AF 33(038)-3736. Permission to publish the data is gratefully acknowledged.

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Thermal Conductivity Method for Analysis of Hydrogen in Steel

by Bruce M. Shields, John Chipman, and Nicholas J. Grant

The vacuum tin-fusion method of analysis for hydrogen, developed by Carney, Chipman, and Grant, has been modified to permit the analysis of the evolved gases for hydrogen by means of a thermal conductivity cell. A properly prepared sample can be analyzed in 10 min with a probable error of ±0.12 ppm. A study of various methods for storage of hydrogen samples shows that samples can be safely held in a dry ice-acetone bath as long as six days. Storage in liquid nitrogen is necessary for samples to be held one week or more.

THE vacuum tin-fusion method, as developed by Carney, Chipman and Grant,[1] is the only analytical procedure which has shown promise of being fast enough for use in the control of hydrogen during steelmaking. It was felt that further simplification and faster speed of operation could be effected by the use of thermal conductivity measurements for analysis of the gases evolved in the tin-fusion method. The application of conductivity measurements to the tin-fusion method is possible because: 1—the evolved gas is essentially a mixture of hydrogen, nitrogen and carbon monoxide with a hydrogen content usually over 50 pct, 2—the evolved gas is collected at a relatively low pressure, and 3—the thermal conductivities of CO and N_2 are practically identical while that of hydrogen is very much greater. The major part of this research program was devoted to the construction and calibration of a vacuum tin-fusion apparatus which analyzes the evolved gases for hydrogen by means of a thermal conductivity cell.

The second phase of the problem was associated with the development of a procedure for storage of samples prior to analysis. With the rapid quenching method for hydrogen sampling,[2] which seems to be the most practical for steel mill use, it is necessary that the samples be stored safely during the interval between sampling and analysis if the hydrogen content of the molten metal is to be maintained in the supersaturated solid samples.

The thermal conductivity bridge has been used for a number of years in the analysis of certain gas mixtures. An elementary discussion of the theory and practice of gas analysis by thermal conductivity measurements is given by Minter.[3] A more comprehensive discussion of the theory and of the various measuring circuits is presented by Daynes.[4] A complete knowledge of the theory and properties of the thermal conductivity of gases and gaseous mixtures can be gained by a study of the standard textbooks on the kinetic theory of gases.[5-7] The existing data on the thermal conductivity of single gases are reviewed by Hawkins,[8] that for a number of binary gas mixtures by Daynes[4] and Lindsay.[9]

The thermal conductivity method may be applied to the determination of the composition of a binary mixture if: 1—the thermal conductivity of the mixture varies monotonically with composition, and 2—the two gases have measurably different thermal conductivities. The greater the difference between the two gases, the greater the sensitivity of the method.[10] The method is applicable to the analysis of multicomponent mixtures when all of the gases in the mixture except one have nearly the same thermal conductivity. Fortunately, the mixture of hydrogen, nitrogen, and carbon monoxide evolved by the tin-fusion analysis[1] falls in this latter classification. The thermal conductivities of nitrogen and carbon monoxide are practically equal; and the thermal conductivity of hydrogen is approximately seven times that of the other two. Therefore, the thermal conductivity of a gaseous mixture of hydrogen, nitrogen, and carbon monoxide at known temperature and pressure can be related directly to the percentage of hydrogen in the mixture by suitable calibration.

Usually the thermal conductivity of a mixture of gases is measured at atmospheric pressure where the thermal conductivity is independent of pressure over a wide pressure range. At very low pressures (below 1 mm Hg), the thermal conductivity of gases varies with the pressure. This phenomenon has been utilized in the Pirani vacuum gage for the measurement of pressures in the range of 10^{-1} to 10^{-4} mm of mercury.[11] Very little has been published concerning the variation of thermal conductivity with pressure at intermediate pressures between 1 mm Hg and 1 atm. However, preliminary measurements indicated that the thermal conductivities did vary with pressure over the range of pressures (up to 10 mm Hg) at which gases are delivered from the vacuum pump. Therefore, the calibration of the thermal conductivity cell had to be planned to include the effects of both gas composition and pressure. Such a calibration chart is shown in Fig. 4.

Most industrial applications of the thermal conductivity method of gas analysis have used a compensated Wheatstone bridge circuit containing two

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This paper is based on a thesis by B. M. Shields submitted in partial fulfillment of the requirements for the Master of Science degree at Massachusetts Institute of Technology.

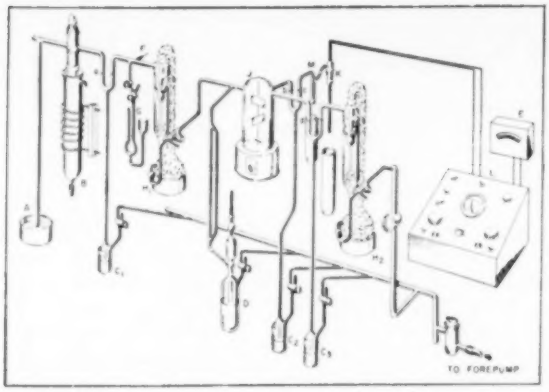

Fig. 1—Apparatus for analysis of hydrogen in steel. A—Mercury lift. B—Furnace. C—Mercury cut-offs. D—McLeod gage. E—Precision ammeter. F—Palladium tube. G—Calibrating pipette. H—Mercury diffusion pumps. J—Mixing chamber. K—Thermal conductivity cell. L—Instrument panel. M—Mercury trap.

or four-cell matched units.[12] Recently Ishihara and Sawa[13] successfully applied a double cell circuit for measuring hydrogen extracted by high temperature vacuum fusion. However, the simplest and theoretically soundest method of measurement utilizes a circuit containing a single thermal conductivity cell[14] maintained at constant temperature. The single conductivity cell circuit was adopted for the vacuum tin-fusion apparatus.

Apparatus

The major modifications to the apparatus of Carney, Chipman, and Grant were the elimination of the copper oxide furnace, the freeze-out traps, and the gas circulating equipment, and their replacement by a conductivity cell, a single cell conductivity bridge, and a mixing chamber. A diagram of the modified apparatus is shown in Fig. 1. Most of the essential parts have previously been described in detail by Carney, Chipman and Grant.[1] A brief description of the new parts is given below.

Known Volume: The known volume extending from the outlet portion of pump H_1 to point b on cut-off C_2 (excluding the conductivity cell) and to point d on cut-off C_3 is equal to 871 ±2 cu cm.

Mixing Chamber: Previous investigators[1] have shown that the hydrogen in the gases evolved during tin-fusion tends to diffuse out sooner and faster than the carbon monoxide and nitrogen. It was noted in fact that the hydrogen which evolved first could collect in the higher portions of the apparatus while the other heavier gases settled in the lower section. Such a stratification could lead to erroneous thermal conductivity results in view of the rapid determinations made with this apparatus. To guard against such an occurrence, a mixing chamber was installed in the system, the details of which are shown in Fig. 2. Experiments with various gases introduced individually in varying orders showed that the mixing chamber eliminates any possibility of stratification.

Thermal Conductivity Cell: The bottom section of the cell is made of pyrex tubing, 1 cm OD and 8 mm ID, with a closed bottom and a female ground joint on the top, as shown in Fig. 2. The seal between the top and bottom sections is made with picein. A thin piece of pure platinum wire, 0.0104 mm (0.0041 in.) in diameter and approximately 16 cm long, is suspended in the center of the cell from nickel wire supports. The wire is held taut by a small tungsten spring. The nickel supports are welded to the tungsten rods used to conduct the current into the cell through a glass-metal seal. The electrical leads from the Wheatstone bridge circuit are attached to the tungsten rods. The entire cell up to the side-arm is maintained at 0°C by immersion in an ice and water bath.

Wheatstone Bridge Circuit: In the single-cell thermal conductivity method, the conductivity cell is kept at constant temperature by immersion in ice and water, and the platinum wire is brought to the same temperature each time by the proper adjustment of the current through the wire. The current needed to maintain the wire at the specified temperature is determined by the rate of heat liberation from the wire, which is the same as the rate at which heat is carried away from the wire by gaseous conduction, provided that other sources of heat loss, such as conduction through the ends of the wire, radiation, and gaseous convection, are negligible. Thus the observed current is a measure of the conductivity of the gas.

A diagram of the single-cell thermal conductivity bridge is presented in Fig. 3. The large bridge rheostat P is set at a resistance such that when the bridge is balanced with pure hydrogen in the cell at the maximum pressure to be encountered, the current passing through the external circuit lies within the range of the precision ammeter A. To balance the bridge with a mixture of hydrogen and other gases at known pressure in the cell, the voltage across the ends of the bridge is adjusted by means of the coarse and fine rheostats Rh_1 and Rh_2. The current recorded on the ammeter can be related to the gas composition after suitable calibration with mixtures of known composition and pressure. It will be noted that virtually all of the current measured by ammeter A passes through the conductivity cell because resistances P and R_2 are so much greater than R_1 and the cell, which has a resistance of approximately 3 ohms. Consequently, very little sensitivity is sacrificed by placing the ammeter in the external circuit where its resistance and temperature variations are not important.

Mercury Trap: The mercury trap between the mixing chamber and the conductivity cell was not originally built into the apparatus. During the calibration it was discovered that the mercury vapor in

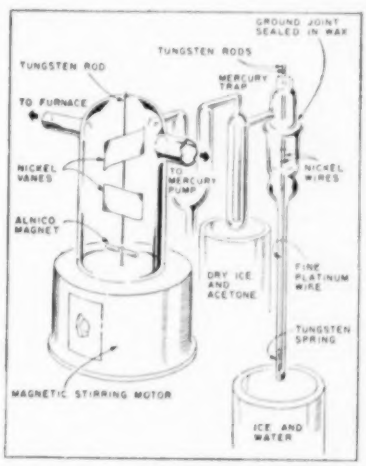

Fig. 2—Detail of mixing chamber and thermal conductivity cell.

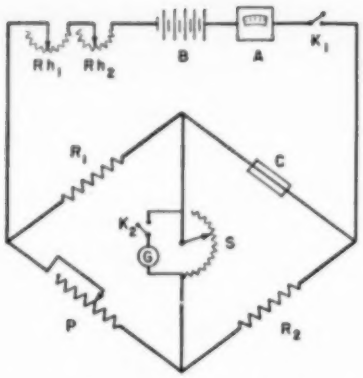

Fig. 3—Diagram of single cell thermal conductivity bridge.

A, precision ammeter, range 0 to 1.000 amp. *B*, battery, four 1½ v dry cells. *C*, thermal conductivity cell. *G*, galvanometer, sensitivity 2 μ amp per division. K_1, main switch. K_2, galvanometer switch. *P*, bridge rheostat, 0 to 1000 ohms. R_1, fixed resistor, 1 ohm. R_2, fixed resistor, 1000 ohms. Rh_1, rheostat, coarse adjustment, 0 to 20 ohms. Rh_2, rheostat, fine adjustment, 0 to 2.5 ohms. *S*, galvanometer shunt.

the vacuum system condensed on the wall of the conductivity cell because it was maintained at a lower temperature than the rest of the system. During a period of two weeks enough mercury condensed upon the wall of the conductivity cell to alter materially the shape of the calibration curves. Damage to the brazed joints was also noted from the mercury present in the cell. The installation of the mercury trap, which is maintained at −80°C by bubbling air through the dry ice-acetone mixture around the trap, eliminated the condensation of mercury vapor in the conductivity cell.

Calibration of Conductivity Cell

It has previously been mentioned that the conductivity of the gaseous mixture in the cell, as measured by the current supplied to the bridge circuit, is a function of both the pressure and the composition of the mixture. Thus, the conductivity cell had to be calibrated with pure gases and mixtures of known composition over a range of measured pressures. Calculations based on a sample size of 1 to 5 g and a hydrogen content in the steel of 1 to 25 parts per million (ppm) indicated that the calibration should cover a pressure range of 0.1 to 3.0 mm of mercury.

A calibration curve of pressure in millimeters of mercury versus conductivity reading in amperes was constructed for pure hydrogen by admitting different amounts of hydrogen into the system through the palladium tube, measuring the pressure in the known volume each time, and determining the current needed to balance the bridge for each pressure. Similar curves were determined for pure nitrogen and pure carbon dioxide by introducing various amounts of the purified gases into the system through the calibrating pipette. The calibration curves are shown in Fig. 4. Because the thermal conductivities of nitrogen and carbon monoxide are practically equal, the calibration curves for the two pure gases are of the same shape and so close together that they can be considered identical. Similar calibration work with gas mixtures of known compositions showed that direct interpolation between the pure gas calibration curves is possible for gas mixtures. Thus a family of calibration curves for mixtures of hydrogen, carbon monoxide, and nitrogen was plotted from 0 to 100 pct H_2 by interpolation between the pure hydrogen curve and the curve representing pure nitrogen (and/or carbon monoxide).

Analytical Procedure

The clear silica crucible is initially charged with about 130 g of chemically pure tin sticks and 0.7 g of purified silicon metal. The crucible is placed in the bottom furnace section, the entire furnace section is assembled, and the system is evacuated. The furnace is gradually heated up to 1050°C and then "baked out" at this temperature for 2 hr. The degassing time and temperature needed for a low blank have been materially reduced by the use of clear silica crucibles and stick tin as compared to using the satin finish silica.

After the completion of the degassing period, the conductivity circuit is standardized. A small amount of hydrogen is admitted to the system through the palladium tube, the pressure of the hydrogen in the known volume is measured with the McLeod gage, and the hydrogen is permitted to enter the conductivity cell. With pure hydrogen at known pressure in the cell, the current is turned on and bridge rheostat *P*, Fig. 3, is adjusted so that, with the bridge balanced, the ammeter reading corresponds to the proper reading for that particular pressure on the pure hydrogen calibration curve. At the completion of the standardization, the cell is turned off and all cut-offs are lowered to evacuate the system in preparation for a blank determination. Normally standardization is only necessary at the beginning of a day's run unless there is reason to suspect that the batteries are becoming weaker or the ambient temperature of the instrument panel changes markedly.

The blank is measured by collecting furnace gas in the known volume for 5 min. The pressure of the blank gas is measured by the McLeod gage, and the percentage of hydrogen in the gas is determined in the conductivity cell. At the completion of the blank determination all the cut-offs are again lowered in preparation for the first analysis.

The metal sample is washed in carbon tetrachloride, dried in a current of dry, oil-free air, and weighed on an analytical balance. It is forced beneath the surface of the mercury reservoir and permitted to float to the top of the mercury column. A strong magnet is used to move the sample over to the furnace head. After cut-offs C_2 and C_3 are raised and the gas mixer is turned on, the sample is dropped into the furnace. At the end of the 5-min collection time, cut-off C_1 is raised and cut-offs C_2 and C_3 are adjusted to points *b* and *d* respectively. The pressure of the collected gas in the known volume is measured with the McLeod gage, preferably in two of the three calibrated sections to detect any water vapor in the gas.* Cut-off C_2 is lowered to permit the gas to enter the conductivity cell and is then raised to point *c*. The conductivity cell is turned on and the bridge circuit balanced by the proper adjustment of coarse and fine rheostats Rh_1 and Rh_2. The percentage of hydrogen in the gas can

* Normally water vapor is only present when samples are improperly dried before analysis or when hollow samples contain water picked up during quenching.

be read off the calibration chart by utilizing the ammeter reading and the previously measured pressure. The conductivity cell is turned off before the cut-offs are again lowered to prevent overheating of the wire in the cell when it is evacuated. All cut-offs are lowered to exhaust the system in preparation for the next analysis.

Evaluation of the Method

Blanks: After an initial 2-hr bake-out period at 1050°C, the 5-min blank value was reduced to about 0.08 ppm for a 2-g sample. The average 5-min blank correction during the analysis of 50 samples with an average weight of 2.9 g was 0.08 ppm. Blank values were determined several times during a day's run and generally showed a gradual decrease throughout the day.

Evolved Gases: A comprehensive discussion of the gases evolved in the tin-fusion method has been presented by Carney, Chipman, and Grant.[1] The gases evolved from the samples analyzed in this study had hydrogen contents of from 65 to 98 pct by volume and averaged close to 90 pct by volume.

Time for Analysis: The time required for the actual analysis of a single sample is 10 min, although in routine use a total time of 15 min per sample is required to allow for sample preparation, weighing, and introduction of the sample into the melt. The total time required to analyze samples on a routine basis can be further reduced from 15 to 12 min per sample by the use of a direct weighing balance and the installation of a faster McLeod gage. However, the 15-min analysis possible with the present apparatus puts it within the range of many steel mill control analyses.

Precision: The overall precision of analysis by the thermal conductivity method was evaluated by the use of duplicate samples. Each of 10 samples, obtained from a molten bath in the manner described by Carney, Chipman, and Grant,[2] was cut in half to provide 10 sets of duplicate samples for analysis. The small size of the samples and the sampling technique make it safe to assume that the two halves of each sample contained equal percentages of hydrogen. The results of the analysis of these duplicate pairs by the tin-fusion method in the thermal conductivity apparatus are summarized in Table I. A statistical analysis of the data from these 10 pairs shows the standard deviation of the error of observation to be ± 0.17 ppm. The probable error is ± 0.12 ppm. Using the statistical criterion of three standard deviations, the error in 95 pct of all analyses will be less than ± 0.5 ppm. It should be emphasized that this precision was obtained with 2 to 3-g samples containing approximately 6 ppm of hydrogen. Greater precision can be obtained when analyzing larger samples.

Storage of Hydrogen Samples

With the rapid quenching method for hydrogen sampling,[2] which preserves the hydrogen content of the molten metal in the supersaturated solid samples, it is necessary that the samples be properly stored to maintain the hydrogen content during the interval between sampling and analysis. Hydrogen is an extremely mobile element and will diffuse out of supersaturated steel samples at room temperature in a relatively short time. Even though the addition of alloying elements to steel may retard the release of hydrogen from quenched samples and although the effusion of hydrogen is slower from austenitic steels than from pearlitic or ferritic steels,[18] it is not possible to maintain the hydrogen content of most liquid steels in a quenched sample for any length of time at room temperature. The work by Carney, Chipman, and Grant[2] includes a complete discussion of storage methods utilized by other investigators together with their own observation that samples could be stored in dry ice for periods of time up to 24 hr with negligible loss of hydrogen. Of the many methods used by previous investigators for either preventing the effusion of hydrogen from the samples or collecting the hydrogen which does diffuse out, the simplest and most practical is the immersion of the samples in a medium at such a low temperature that the diffusion of hydrogen is virtually stopped. It was the purpose of this investigation to determine what storage temperature was necessary to inhibit effectively the effusion of hydrogen from steel samples and how long the samples could be stored at this temperature before a measurable loss of hydrogen occurred.

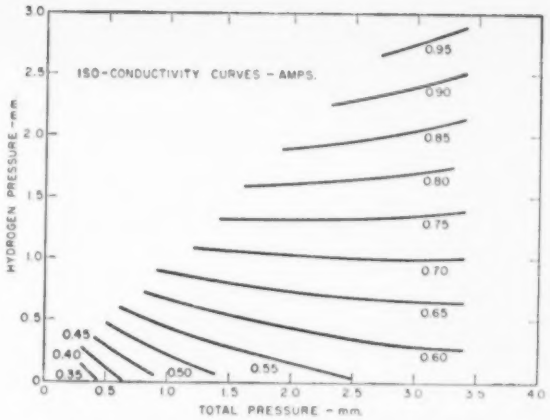

Fig. 4—Calibration curves for conductivity cell.

The samples for this investigation were obtained from heats melted in the controlled atmosphere furnace previously described in detail,[2] under a mixture of 5 to 10 pct H_2 and the balance helium. The details of the sampling procedure, utilizing a modified Taylor sampling device, have also been described. After thorough quenching in water and then in a dry ice-acetone bath some of the samples were stored in a dessicator at room temperature,

Table I. Precision of Analysis by Duplicate Samples

Sample No.	First Analysis, Ppm	Second Analysis, Ppm	D	$(\overline{D}' - D_i)^2$
9	6.74	6.64	0.10	0.0100
10	6.36	5.92	0.44	0.1936
11	6.42	6.95	0.53	0.2809
12	6.04	5.82	0.22	0.0484
14	6.43	6.45	0.02	0.004
21	6.10	5.94	0.16	0.0256
23	5.59	5.63	0.04	0.0016
25	5.96	6.01	0.05	0.0025
00	7.24	7.09	0.15	0.0225
00	5.16	5.31	0.15	0.0225
				0.6080

σ_D = Standard deviation of the difference.
σ_a = standard deviation of the error of observation.
P.E. = probable error (assuming normal distribution).

$$\sigma_D = \sqrt{\frac{\Sigma\,(\overline{D}' - D_i)^2}{n}} = \sqrt{0.0608} = 0.2466.$$

$$\sigma_a = \frac{\sigma D}{\sqrt{2}} = 0.1744 \text{ ppm.}$$

$$P.E. = 0.6745\ \sigma_a = 0.1176 \text{ ppm.}$$

some in an ice and water bath, some in a dry ice-acetone mixture, and the rest in liquid nitrogen.

Prior to analysis, the samples were removed briefly from the storage baths one at a time and cut into 2 to 4-g specimens on an underwater cut-off wheel filled with ice water. After cutting, the specimens were dried and returned to their original storage bath. Throughout the cutting operation suitable precautions were observed to prevent contamination of specimens with grease, oil, or other materials likely to contain hydrogen.

The samples were analyzed according to a time schedule which depended upon the particular storage method being investigated. The results of the analyses for the four storage methods are shown in Tables II to V.

The data in Table II show that it is not safe to keep quenched hydrogen samples at room temperature. The ferritic Armco iron samples used in this investigation showed a gradual decrease in hydrogen content beginning almost immediately after the quenched samples had reached room temperature.

Storage in an ice-water mixture does not retain the hydrogen content much better than does room temperature storage. The analyses reported in Table III indicate that hydrogen samples cannot be stored even one day at 0°C without losing an appreciable portion of their hydrogen content.

It is apparent from the data in Table IV that storage in a dry ice-acetone mixture is satisfactory for periods of time up to six days. If samples are to be stored for as long as a week or more, they must be kept in liquid nitrogen.

It should be emphasized that the results quoted in this study were determined only for Armco iron samples containing about 6 ppm of hydrogen.

Table II. Effect of Time on the Loss of Hydrogen from Samples Stored in Dessicator at Room Temperature (25°C)

Storage Time, Hr	Hydrogen Content, Ppm	Average, Ppm
1	7.8	8.1
1	8.3	
2	7.1	7.7
2	8.2	
6	6.2	6.5
6	6.8	
17	5.6	5.4
17	5.2	

Table III. Effect of Time on the Loss of Hydrogen from Samples Stored in Ice and Water Bath, 0°C

Storage Time, Hr	Hydrogen Content, Ppm	Average, Ppm
4	6.1	6.0
4	5.9	
27	2.8	3.2
27	3.5	
49	2.6	2.5
49	2.3	
73	3.1	

Table IV. Effect of Time on the Loss of Hydrogen from Samples Stored in Dry Ice-Acetone Mixture, —78°C

Storage Time, Day	Hydrogen Content, Ppm	Average, Ppm
1	6.8	
1	5.9	
1	6.1	6.2
2	7.2	
2	6.7	
2	6.6	
2	7.1	6.9
4	6.4	
4	5.6	
4	5.6	
4	6.9	6.1
8	6.6	6.6
10	5.2	
10	5.2	
10	5.3	5.2

Table V. Effect of Time on the Loss of Hydrogen from Samples Stored in Liquid Nitrogen, —196°C

Storage Time, Day	Hydrogen Content, Ppm	Average, Ppm
1	6.4	
1	6.2	
1	6.0	
1	6.4	
1	6.0	6.2
2	6.0	
2	7.2	6.6
4	6.0	
4	6.4	
4	5.9	
4	5.8	6.0
6	6.5	6.5
10	6.1	
10	7.1	
10	5.9	6.4

It should be emphasized that the results quoted in this study were determined only for Armco iron samples containing about 6 ppm of hydrogen.

Summary

The vacuum tin-fusion method of analysis for hydrogen, developed by Carney, Chipman, and Grant, has been modified to permit the analysis of the evolved gases for hydrogen by means of a thermal conductivity cell. The major advantages of the thermal conductivity method are: 1—elimination of the often questionable conversion of hydrogen to water vapor in the copper oxide furnace, 2—simplification of apparatus, and 3—increased speed of analysis. A properly prepared, weighed sample can be analyzed in 10 min with a probable error of ± 0.12 ppm of hydrogen.

A study of various methods for storage of hydrogen samples shows that samples can be held in a dry ice-acetone bath as long as six days with negligible loss of hydrogen. Storage in liquid nitrogen is necessary for samples to be held one week or more.

Acknowledgments

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Reduction of Silicon from Blast Furnace Type Slags

by James C. Fulton, Nicholas J. Grant, and John Chipman

This paper contains data on the distribution of silicon between liquid iron-silicon-carbon alloys saturated with respect to graphite and CaO-SiO_2-Al_2O_3 slags under 1 atm of CO at 1600°C. The ranges of slag compositions studied were extended from the dicalcium silicate saturated liquidus composition up to silica concentrations at which SiC appeared as a stable phase.

IN blast furnace operation it is not to be expected that slag and metal reach equilibrium with one another. Nevertheless, the silicon content of the metal varies with slag composition and with temperature in a manner which would be predicted from equilibrium considerations. Similarly, the distribution of sulphur between slag and metal does not attain an equilibrium state, yet the influence of slag composition is strongly analogous to its effect on the distribution equilibrium.

The desulphurizing power of metallurgical slags has been shown to be highly dependent upon the FeO content of the slag. Moreover, the rate of removal of sulphur from slags is influenced by the oxygen potential of the slag-metal system. Thus it was shown by Grant, Kalling, and Chipman[1] that the presence of MnO in slags which are low in FeO causes a marked slowing down of the transfer of sulphur from metal to slag.

This led to the hypothesis that the slow removal of sulphur by blast furnace slags of more acid composition might be due in part to the effect of SiO_2 on the oxygen potential of the system. This was verified in the work of Grant, Troili, and Chipman,[2] who found that the desulphurizing power of the more acid blast furnace slags could be markedly improved by an increase in the silicon content of the underlying metal. Their explanation of this improvement was that the higher silicon content of the metal decreased the rate of transfer of more silicon and, along with it, of oxygen from the slag to the metal. The slowness of the transfer of sulphur from metal to slag was the result of the slow reduction of SiO_2 from slag to metal. Attempts to study the rate of sulphur removal had in the past resulted in very slow rates corresponding to the rates of silica reduction. It has become evident on the basis of these studies that further experimental studies on the rate of removal of sulphur must take these factors into consideration if there is to be a clear understanding of the rate of sulphur transfer under conditions simulating those existing in the blast furnace. It will be necessary, at least in a part of such study, to employ combinations of slag and metal in which the disturbing effect of silica reduction has been eliminated; in other words, to employ slag-metal combinations which are already in equilibrium with respect to the transfer of silicon.

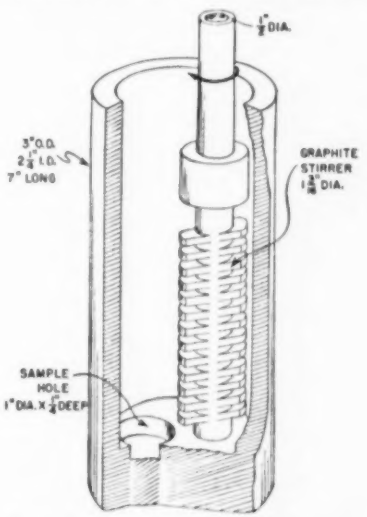

Fig. 1—Schematic drawing of graphite crucible and stirrer.

In preparation for such studies of desulphurization, a preliminary program of research on the distribution of silicon between slag and metal has been undertaken. This will ultimately include a comprehensive survey of the effects of temperature and slag composition on the equilibrium distribution of silicon between slag and metal. The present paper is a report on experimental methods employed and on

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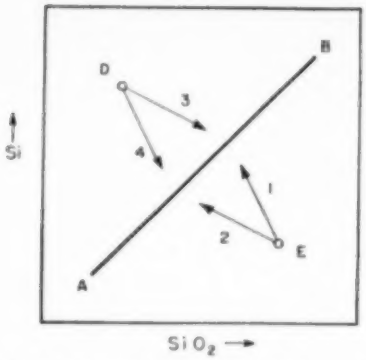


Fig. 2—Schematic representation of changes in composition during reaction. Lines 1 and 2 represent Eq. 1 as written. Lines 3 and 4 represent the reverse reaction.

the results obtained in one series of slag compositions at 1600°C.

Experimental Procedure

The furnace used in this investigation has been adequately described.[6] The crucible design, initially modified by Grant, Kalling, and Chipman,[1] was used in the first 42 heats of the current study. Beginning with heat 43, the crucible and stirrer arrangement shown in Fig. 1 was substituted. The new design was shown to have not only good thermal characteristics, but also somewhat better mixing qualities.

The temperature of the present set-up is controlled by sighting an optical pyrometer down through the hollow stirring rod and into a centrally drilled ⅜ in. diam hole in the stirrer. The hole ends 1 in. from the bottom of the stirrer at a point just below the slag-metal interface. By means of a Pt-Pt-Rh thermocouple inserted into the crucible while the stirrer was turning at the usual rate of 600 to 800 rpm, it was found that a temperature difference of not more than 6°C exists between the bottom of the crucible and upper slag surface. Similarly, a thermocouple placed in the pyrometer sighting hole checked the temperature of the optical pyrometer within ±2°C. These calibrations served to substantiate the accuracy of the temperature measurements and reaffirm the conclusions of previous investigators who used this apparatus. The main source of temperature fluctuation was the normal variation in control of the induction furnace, yielding a maximum deviation of ±10°C throughout a heat.

The metals used in the heats are listed in Table I. The Armco iron punchings have been used throughout all runs while the source of silicon has changed. In the study of the CaO-SiO_2 slags, silicon metal (A) was used in heats 5, 6, 7, 8, 9, and 12 while silicon metal (B) was used in the remainder of these heats. For the CaO-SiO_2-Al_2O_3 slags, silicon metal (A) was used in all heats up to 97, at which time a 44 pct silicon ferro-alloy was prepared with Armco iron and

Table I. Composition of Iron and Silicon Used in Charge

Armco Iron	Silicon (A)	Silicon (B)	Silicon (C)
0.029 pct C	1.62 pct Fe	0.20 pct	0.90 pct Fe
0.017 pct Mn	1.50 pct Al	(max	0.08 pct Al
0.004 pct P	0.14 pct Ti	impurities)	
0.017 pct S	96.74 pct Si	99.80 pct Si	98.70 pct Si
	(by difference)	(by difference)	

Table II. Chemical Analyses of Slag-Metal Samples for CaO-SiO_2 Slags at 1600°C

Heat and Sample No.	Time at Temperature,* Hr	[Pct Si]	(Pct SiO_2)	(Pct CaO)
F5	Charge	4.8	55.8	44.2
–1	1.25	5.37	52.36	
–2	2.25	6.47	51.09	
–3	3.25	6.95	50.20	
–4	4.25	7.38	49.34	
–5	5.25	7.82	48.68	
F6	Charge	19.9	50.0	50.0
–1	2.0	20.43	48.03	
–3	4.0	20.21		
–5	6.0	20.60	46.67	
F7	Charge	9.8	44.0	56.0
–1	1.25	9.59	43.37	
–3	3.25	10.14		
–5	5.25	10.42	42.37	
F8	Charge	9.8	59.8	40.2
–1	1.17	13.98	54.62	
–2	2.17	15.14	53.15	
–3	3.17	15.74	51.30	
–4	4.17	16.50	50.37	
–5	5.17	16.79	49.19	
–6	6.17	16.87	48.76	
F9	Charge	14.8	55.8	44.2
–1	1.50	16.33	54.34	
–2	2.50	17.10	51.62	
–3	3.50	17.88	50.55	
–4	4.50	18.26	49.59	
–5	5.50	19.00	48.83	
F12	Charge	21.0	59.8	40.2
–2	1.0	19.00	59.36	
–3	12.0	22.23	51.27	
–4	18.0	21.78	50.78	
–5	18.0	21.56	50.73	
–6	23.0	22.44	48.92	
–7	23.0	22.00		
–8	24.0	22.25	48.62	
–9	24.0	22.29		
F31	Charge	23.0	50.0	50.0
–1	1.5	22.18	50.02	48.75
–2	2.5	22.80	49.44	
–3	8.0	21.74	50.34	49.52
–4	10.0	22.84	50.08	
–5	12.0	21.88	50.24	48.85
F32	Charge	21.0	43.0	57.0
–1	1.08	19.96	43.91	
–2	2.92	19.95	44.04	
–3	7.17	20.05	44.08	
–4	9.33	20.06	44.28	
–5	11.33	19.52	44.02	
F43	Charge	21.8	49.0	51.0
–1	1.0	21.16	48.15	
–2	8.0	21.42	47.87	
–3	9.0	21.84	47.17	
–4	9.5	22.06	47.48	
F44	Charge	21.6	47.3	52.7
–1	1.0	18.63	47.68	
–2	4.0	19.23	46.92	
–4	6.0	19.25	45.68	
–6	8.0	19.07	46.05	
F47	Charge	23.0	52.0	48.0
–1	1.0	22.14	51.18	
–2	3.0	23.00	51.24	
–4	6.0	22.58	50.80	
–5	7.0	23.28		
–6	8.0	22.59	51.22	
F74	Charge	15.3	45.5	54.5
–1	1.0	14.94	45.52	
–5	8.0	15.43	44.28	
F75	Charge	17.9	43.5	56.5
–1	1.0	17.52	43.48	
–5	8.0	17.38	44.04	55.39
F81	Charge	23.0	44.0	56.0
–1	1.0	22.34	44.68	
–3	5.0		44.52	
–5	8.0	22.15	45.40	54.47
F82	Charge	11.8	42.6	57.4
–1	1.0	11.57	42.64	
–3	5.0		42.84	
–5	8.0	11.93	42.76	56.11
F96	Charge	23.0	47.0	53.0
–2	2.0	22.20	46.40	
–3	5.0	22.26		
–4	7.0		46.50	
–5	8.0	22.09	46.30	51.80

* Zero time is taken as that time when the slag and metal are first judged to be molten and at the reaction temperature. The time listed is the time after zero time.

silicon metal (B). This alloy was used in all subsequent heats.

The slags were made by mixing master slags which had been prefused in a graphite crucible. Actual chemical analyses after fusion were used in calculating the various quantities desired.

The "zero-time" used in the tables and figures is a somewhat ambiguous quantity since liquid metal and liquid slag were not mixed to start a run. Si and SiO_2 analyses tended to stray from the calculated composition when samples were taken prior to half an hour after all constituents were in the crucible at 1600°C. For the first 101 heats, about half of the slag and all the metal were placed in the crucible and heated to 1600°C in an atmosphere of carbon monoxide which was purified by passing over ascarite and anhydrone. (Nominal gas purity was 97 pct CO, 3 pct N_2.) Generally, it required 15 min to heat the charge to 1600°C and about 10 min more for it to melt in so that the remaining portion of the slag could be added. "Zero-time" for the first 101 heats was taken as that time when all the slag and metal were in the crucible and at the reaction temperature. This is obviously not "zero" reaction time.

Beginning with run 102, a change in melting procedure was made to try to reduce the length of time necessary to fuse the slag as well as to help stabilize the initial silicon analysis. The new procedure consisted of melting only the metal in a nitrogen atmosphere and allowing 5 to 10 min for graphite saturation. All the slag was then added within 5 min, and as soon as the system reached the reaction temperature, the run was considered started. In this procedure the CO atmosphere was established simultaneously with the slag addition. "Zero-time" was again taken when all constituents reached the reaction temperature.

The course of the reaction was followed by slag and metal samples removed during a run. The slag samples were solidified on the end of an iron rod and metal samples were drawn up into a Vycor tube with an aspirator bulb. Slag and metal samples were crushed to −100 mesh. Iron particles were removed from the slag by a hand magnet prior to analysis.

Table III. Chemical Analyses for Slag-Metal Samples for CaO-SiO_2 and 10 Pct Al_2O_3 at 1600°C

Heat and Sample No.	Time at Temperature,* Hr	[Pct Si]	(Pct SiO_2)	(Pct CaO)	(Pct Al_2O_3)
F49	Charge	18.9	37.7	51.8	10.5
−1	1.0	15.51	37.80		
−3	5.0	15.22	37.58		
−6	8.0	15.02	38.63		10.60
F50	Charge	22.9	51.3	38.1	10.6
−1	1.0	19.42	48.03		
−3	5.0	20.68	46.05		
−5	7.0	20.68	45.28		
−6	8.0	20.71	45.46	42.24	12.84
F61	Charge	13.8	40.0	50.0	10.0
−1	1.0	13.49	39.00		
−3	5.0	13.50	39.08		
F69	Charge	9.7	41.0	50.0	9.0
−1	3.0	9.67			
−2	5.0	9.86			
−3	7.0	9.93	40.08	49.25	9.64
F72	Charge	14.8	43.0	47.0	10.0
−1	1.0	15.03	41.64		
−5	8.0	15.10	41.12	47.48	11.08
F73	Charge	21.9	43.0	47.0	10.0
−1	1.0	21.65	41.60		
−5	8.0	21.52	42.56	47.45	10.12
F79	Charge	17.9	42.0	48.0	10.0
−1	1.0	18.03	38.96		
−3	5.0		38.68		
−5	8.0	17.96	38.76	49.77	11.20
F80	Charge	23.9	44.0	46.5	9.5
−1	1.0	23.12	43.84		
−3	5.0		44.04		
−5	8.0	23.09	43.84	45.68	10.64
F85†	Charge	19.9	40.0	49.5	10.5
−1	1.0	19.70	39.04		
−3	5.0	19.54	40.40		
−5	8.0	19.36	41.16	47.74	11.56
F97	Charge	18.9	43.0	47.0	10.0
−2	2.0	18.54	42.36		
−3	5.0	18.80			
−5	8.0	18.55	42.65	47.59	9.98
F98	Charge	6.2	38.0	52.1	9.9
−2	2.0	6.42	37.24		
−3	5.0	6.57			
−5	8.0	6.77	36.56	52.50	11.08
F106†	Charge	19.0	44.4	45.7	9.8
−2	2.0	19.33	43.68		
−3	4.5	19.34			
−5	7.0	19.33	43.56	46.42	9.88
F117†	Charge	7.5	35.5	54.2	10.3
−2	2.0	7.84	36.95		
−3	5.0	8.04			
−5	8.0	8.10	36.30		10.65
F118†	Charge	21.0	47.0	43.5	9.5
−1	1.0	23.20	47.00		
−3	5.0	23.07			
−5	8.0	22.92	46.50		10.66
F123†	Charge	15.0	44.0	46.5	9.5
−1	1.0	16.71	43.75		
−3	5.0	17.08			
−5	8.0	17.35	42.72		11.00
F125†	Charge	10.0	36.0	53.5	10.5
−1	1.0	10.23	36.84		
−3	4.0	10.24			
−4	6.0	10.35	36.68		11.52

* See Table II.
† CO bubbled through metal and slag, in all other heats CO flushed over slag surface.

Reaction Studied

The chemical reaction under investigation is given in Eq. 1:

$$SiO_2\ (slag) + 2C\ (gr) = \underline{Si} + 2CO\ (g) \quad [1]$$

The SiO_2 was dissolved in a CaO-SiO_2 or CaO-SiO_2-Al_2O_3 slag. The metal phase consisted of Fe and Si saturated with graphite.

If a system is considered which is composed of a CaO-SiO_2 slag and the corresponding metal, there are five components and four phases. The components are Ca, Si, O, Fe, and C. The phases are slag, metal bath, gas, and graphite. According to the phase rule this yields two degrees of freedom in a constant pressure system. Thus, if the temperature and the percentage of silicon is fixed, the equilibrium state of the system will be completely described.

Fig. 2 shows schematically how the reaction progresses. Assume line *AB* represents the equilibrium distribution of Si and SiO_2, at a given temperature. If the initial composition *E* is selected, there will be silica reduction; that is, Eq. 1 shows a net reaction toward the right (increasing silicon in the metal) along a path such as 1 or 2 in Fig. 2. If an initial composition such as *D* is selected, there will be silicon oxidation, and Eq. 1 will show a net reaction to the left (increasing SiO_2 content) indicated by path 3 or 4. The steepness of the path from the initial composition depends on the relative quantities (weights) of the two phases charged. Paths 2 and 3 represent higher weight ratios of metal to slag than paths 1 and 4.

Finally, it may be pointed out that these paths are not straight. As the reaction proceeds in either direction, there is a transfer of material between the slag and metal phases tending to increase the weight of the one relative to the other. When silica reduction occurs, there is a loss of 1 g of SiO_2 from the slag for each gain of 28/60 g of silicon in the metal.

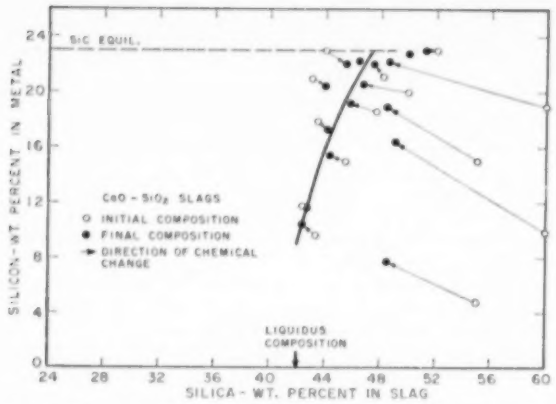


Fig. 3—Silicon distribution at 1600°C for Fe-Si-C alloys saturated with graphite and in contact with $CaO-SiO_2$ slags under 1 atm of CO. CO gas flushed over slag surface.

Since the iron is saturated with graphite, the only change of percentage of carbon in the metal is that due to the corresponding change of percentage of silicon. In other words, carbon changes due to solubility effects, not stoichiometric considerations.

Results and Discussion

The results of chemical analyses of slag and metal samples taken from heats held at 1600°C are shown in Tables II, III, and IV and are plotted in Figs. 3, 4, and 5 for 0, 10, and 20 pct Al_2O_3, respectively. The final compositions of the binary slags of Fig. 3 are those listed in Table II. The ternary slags of Figs. 4 and 5 have been corrected to even 10 and 20 pct Al_2O_3 as explained below. From preliminary curves similar to Figs. 4 and 5 it was evident that an increase from 10 to 20 pct Al_2O_3 led to a corresponding decrease of from 2 to 7 pct SiO_2, depending on the silicon level. In plotting the final points, therefore, a proportional adjustment was made in the percentage of SiO_2 to correspond to exactly 10 or 20 pct Al_2O_3. This adjustment was not made in the initial points.

Chemical analyses have shown the usual variations for this type of determination. In run 12, Table II, duplicate samples were taken at 18, 23, and 24 hr. The silicon analyses showed a maximum deviation of 0.44 pct Si and the only slag pair that was analyzed in duplicate indicated a deviation of 0.05 pct SiO_2. In run 31, Table II, the silicon dropped 1.06 pct Si from sample 2 to 3 in a run that is not changing composition according to the slag analysis. Thus, there are rather wide variations of results possible due to experimental errors. A more dependable measure of the limits of error can be found in time-averages of the Si and SiO_2 analyses. In general, these plots indicate a deviation of ± 0.20 pct Si and ± 0.30 pct SiO_2 for any one run.

Material balances on some of the runs indicated serious discrepancies between the SiO_2 lost from the slag and the Si gained by the metal. Table V shows the result of such balances made on runs 5, 8, 9, and 12 (see Fig. 3 and Table II). The charge compositions of slag and metal were taken as the initial conditions. From the final SiO_2 analyses, corresponding

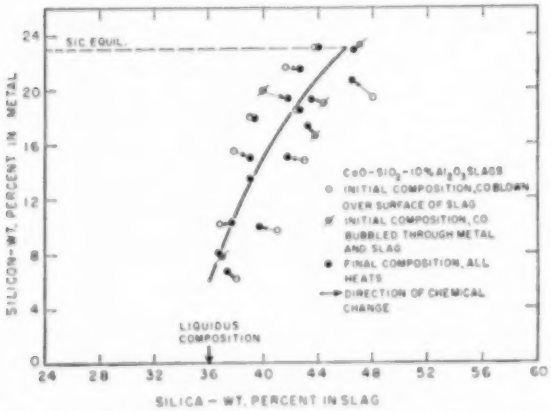

SiC EQUIL.
CaO-SiO2-10%Al2O3 SLAGS
INITIAL COMPOSITION, CO BLOWN OVER SURFACE OF SLAG
INITIAL COMPOSITION, CO BUBBLED THROUGH METAL AND SLAG
FINAL COMPOSITION, ALL HEATS
DIRECTION OF CHEMICAL CHANGE
LIQUIDUS COMPOSITION
SILICON-WT. PERCENT IN METAL
SILICA - WT. PERCENT IN SLAG

Fig. 4—Silicon distribution at 1600°C for Fe-Si-C alloys saturated with graphite and in contact with $CaO-SiO_2$-10 pct Al_2O_3 slags under 1 atm of CO.

Table IV. Chemical Analyses for Slag-Metal Samples for $CaO-SiO_2$ and 20 Pct Al_2O_3 at 1600°C

Heat and Sample No.	Time at Temperature,* Hr	[Pct Si]	(Pct SiO_2)	(Pct CaO)	(Pct Al_2O_3)
F52	Charge	18.9	40.0	40.8	19.2
—1	1.0	18.72	39.78		
—3	5.0	18.78	40.01		
—5	7.0	18.82	39.81	40.71	19.32
F54	Charge	16.8	30.0	50.0	20.0
—1	1.0	16.43	30.44		
—3	3.0	16.60	31.12		
—5	5.0	16.23	31.60		
—6	6.0	16.04	31.80	48.69	19.64
F66	Charge	3.8	30.0	50.0	20.0
—1	1.0	3.91	31.28		
—3	5.0	4.05	30.48		
—6	8.0	4.18	29.64	49.10	20.72
F70	Charge	20.9	44.0	37.0	19.0
—1	1.0	21.07	42.08		
—5	8.0	20.87	42.20	38.04	20.04
F76	Charge	6.2	29.6	50.0	20.4
—1	1.0	6.34	29.46		
—4	7.0	6.46	29.36	49.11	20.28
F78	Charge	11.8	38.0	42.0	20.0
—1	1.0	11.94	37.84		
—3	5.0	12.08			
—5	8.0	12.30	36.92	43.36	19.60
F86†	Charge	11.8	32.0	48.0	20.0
—1	1.0	11.66	31.92		
—3	5.0	11.72	32.12		
—5	8.0	11.70	31.80	47.41	19.24
F87†	Charge	8.8	28.0	52.0	20.0
—1	1.0	8.55	27.72		
—3	5.0	8.43	28.04		
—5	8.0	8.62	28.72	49.78	19.52
F92	Charge	13.8	36.0	44.5	19.5
—2	2.0	13.96	35.32		
—3	5.0	14.08	35.24		
—5	8.0	14.18	34.98	43.90	19.80
F103†	Charge	7.8	33.1	47.7	19.2
—2	2.0	8.34	30.88		
—3	5.0	8.46			
—5	8.0	8.23	30.52	49.77	19.92
F107†	Charge	18.0	35.5	44.0	20.5
—2	2.0	19.48	35.96		
—3	5.0	19.43			
—5	8.0	19.32	36.52	43.41	20.64
F109†	Charge	22.0	45.0	35.2	19.8
—2	2.0	22.86	43.28		
—3	5.0	22.52			
—5	8.0	22.62	43.72	36.44	20.68
F120†	Charge	15.0	32.0	47.8	20.2
—1	1.0	16.76	32.36		
—3	5.0	16.43			
—5	8.0	16.38	33.59		20.97
F121†	Charge	22.0	40.0	39.7	20.3
—1	1.0	23.77	36.41		
—3	5.0	23.47			
—5	8.0	23.20	40.43		21.68
F124†	Charge	6.0	29.0	51.0	20.0
—2	2.0	6.26	29.08		
—3	5.0	6.30			
—5	8.0	6.35	29.60		21.28

* See Table II.
† See Table III.

Si analyses have been calculated, neglecting the weight of slag and metal removed by sampling. Even such checks had limited value. For example, 5 and 12 lost slag due to copious CO evolution which frothed the slag into the system above the crucible. Run 12 is also low in Si for the additional reason that silicon carbide formed as one of the stable phases, as will be explained later.

Pin-pointing the initial composition has been a tedious problem. There are a number of factors that contribute to this uncertainty: 1—lack of homogeneity of master slags, 2—contaminated crucibles from previous runs, 3—dusting losses of slag, 4—errors in weighing, and 5—contamination of metal by entrapped slag. In view of these experimental difficulties, the first sample analyzed, instead of the charged composition, was plotted as the initial composition in Figs. 3 to 5, except when the results extrapolated back to the calculated composition. The final compositions are those listed in Tables II to IV.

It is important that significant chemical changes are detected, for it is the direction of the change as well as the final composition that determines the position of the curves. The greatest difficulty in interpolation of the curves in Fig. 3 to 5 was due to the broad gap remaining between the very slowly converging points from two sides. Silica reduction and silicon oxidation are very slow processes, even at concentrations rather far removed from equilibrium when from 8 to 24 hr were taken to approach equilibrium with vigorous stirring of the slag and metal. This was well illustrated in the curves shown by Grant, Troili, and Chipman.[2] Probably the most significant factor in limiting the accuracy of the distribution curves in Figs. 3 to 5 is this sluggishness of the reaction. It seems to place the limits of the distribution curves at ±1 pct SiO_2 at a given silicon concentration.

The range of SiO_2 concentrations available for study in this investigation were found to be determined by two factors. At the low SiO_2 end, the study was terminated by the liquidus compositions at which dicalcium silicate precipitates. The arrows pointing downward on the abscissas of Figs. 3, 4, and 5 at 42, 36, and 29 pct SiO_2, respectively, represent the liquidus compositions as read from the CaO-SiO_2-Al_2O_3 phase diagram.[4]

As SiO_2 was increased to the upper limit, it was found that the system became saturated with respect to silicon carbide (SiC) when the metal contained 23.0 pct Si, according to the reaction:

$$\underline{Si} + C\ (gr) = SiC\ (solid) \qquad [2]$$

The SiC has been identified by X-ray patterns of specimens from the slag and metal and by metallographic examination of metal specimens. Comparison with previous studies on the structure of SiC[5-7] revealed that the β modification was formed. It appeared in various colors with blue and green predominating.

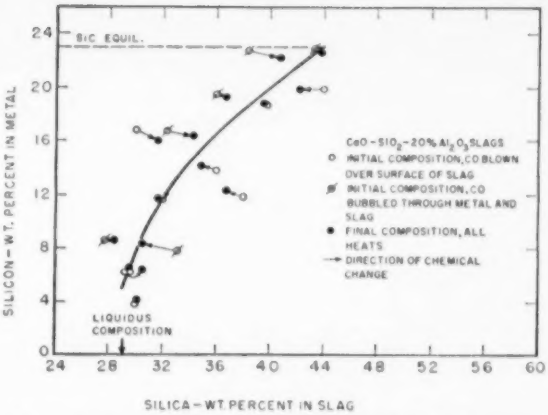
The addition of another phase (SiC) to the system, in addition to those listed above, decreases the number of degrees of freedom by one. For the binary slags (Fig. 3), there is now only one degree of freedom, namely, temperature. For the ternary slags (Figs. 4 and 5), two degrees of freedom remain, namely, temperature and percentage of Al_2O_3. By fixing the temperature and percentage of Al_2O_3 at 0, 10, and 20 in Figs. 3, 4, and 5, respectively, these systems are completely described. The data are summarized in the three curves of Fig. 6 which extend from the dicalcium silicate liquidus to termini at 23 pct Si, where SiC appears.

It is interesting to compare the present data with the electrochemical study of Chang and Derge.[8] Briefly, their experimental apparatus consisted of a silicon carbide electrode dipped into a slag held in a graphite crucible. The electromotive force between the graphite and silicon carbide was taken as a measure of the silica activity in the slag. Fig. 7 shows a summary of their data at 1600°C where they have plotted iso-electromotive force (iso-activity) lines as a function of slag composition.

In order to get some comparable results from the present study, it is necessary to return to Eq. 1 and the corresponding equilibrium constant which is

$$K_1 = \frac{a_{Si}\, p^2_{CO}}{a_{SiO_2}}$$

Since the metal is saturated with carbon, and the


SiC EQUIL.
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DIRECTION OF CHEMICAL CHANGE
LIQUIDUS COMPOSITION
SILICON - WT. PERCENT IN METAL
SILICA - WT PERCENT IN SLAG

Fig. 5—Silicon distribution at 1600°C for Fe-Si-C alloys saturated with graphite and in contact with CaO-SiO_2-20 pct Al_2O_3 slags under 1 atm of CO.

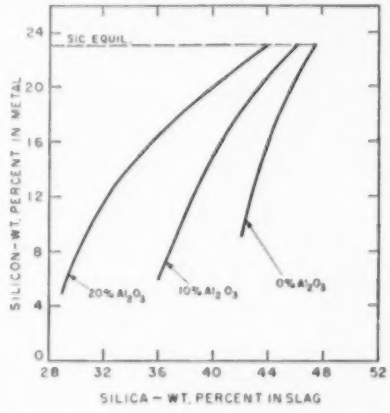

Fig. 6—Summary of silicon distribution curves at 1600°C for liquid Fe-Si-C alloys saturated with graphite and in equilibrium with CaO-SiO_2-Al_2O_3 slags under 1 atm of CO.

Table V. Material Balances on Runs 5, 8, 9, and 12

Run No.	Final Pct Si Observed	Final Pct Si Calculated
5	7.82	9.46
8	16.87	16.9
9	19.00	18.9
12	22.27	28.6

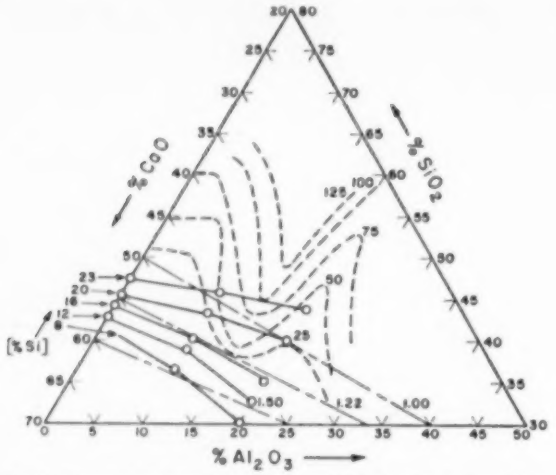

Fig. 7—Ternary isothermal section at 1600°C showing a comparison of iso-activity curves for silica. Dashed lines are electromotive force measurements, Chang and Derge.[8] Solid lines are silicon distribution, authors. Long and short dashed lines are lime-silica ratios.

pressure of carbon monoxide is constant, any alloy with a given silicon content will have a fixed silicon activity. Thus, if the slag compositions for constant silicon concentration in the metal are picked off Figs. 3 to 5, these points will represent constant silica activities. In this way, lines of constant silica activity corresponding to constant silicon concentrations have been superimposed on the results of Chang and Derge in Fig. 7. It is evident that no agreement exists between the two sets of data. It is the authors' view that the disagreement stems from the interpretation which Chang and Derge put upon their data. A more detailed discussion seems premature at this time and will be deferred until after publication of current work on the activity of silicon in Fe-Si-C alloys.

Based on the lines representing our results in Fig. 7, the following statements may be made concerning the activity of SiO_2: 1—at constant percentage of silica, its activity increases with increasing Al_2O_3 and decreases with increasing CaO; 2—the activity of SiO_2 is strongly dependent upon the lime:silica ratio. At a ratio of about 55:45 it is independent of Al_2O_3 or other composition variables. At lower ratios it is decreased and at higher ratios increased by addition of Al_2O_3. Lines of constant lime:silica ratio have been constructed on Fig. 7 to show this relation.

The question of the rate-controlling step in reaction 1 has been raised by Darken[9] with respect to the retarding action of SiO_2 reduction on desulphurization in blast furnace type slags. It was suggested that perhaps the rate is controlled by lack of gas bubble nucleation at the slag-metal interface. While most of the heats have been made with CO gas flushing over the slag surface, a sufficient number have been made in which CO was bubbled through the slag and metal in order to be able to detect any appreciable differences. All heats in Fig. 3 had CO flushing over the surface, while a differentiation of the method of gas entrance was made for the heats in Figs. 4 and 5. Qualitatively it appears that there was no improvement of rate by provision of artificial gas bubble nuclei. The similarity of results may be due to the intimate mixing of metal, slag, and gas by the stirring mechanism.

Sawamura and Sawamura[10] recently published some results for the equilibrium of liquid pig iron with CaO-SiO_2-Al_2O_3 slags containing 10 pct Al_2O_3. These workers used small heats consisting of approximately 15.5 g of metal and 6 g of slag. A graphite crucible containing the melt was quenched in water at the end of a run. Their results were not tabulated; however, the plot of a run at 1600°C indicated that equilibrium was obtained with 3.3 pct Si for a slag containing 44 pct SiO_2, 46 pct CaO, and 10 pct Al_2O_3. In the present investigation, this same slag was found to require 20.7 pct Si. From their graph it is obvious that silica reduction is still in progress at the end of 4 hr, but they relied on the more slowly changing silicon analyses. It is also worth noting that Sawamura and Sawamura did not stir their heats. This immediately suggests that diffusion of silicon in the metal or of silica in the slag may have been the rate-controlling step.

Conclusions

The results of this investigation may be summarized as follows:

1—The distribution of silicon between graphite-saturated Fe-Si-C alloys in equilibrium with CaO-SiO_2 and CaO-SiO_2-Al_2O_3 slags containing 10 and 20 pct Al_2O_3 has been established at 1600°C under 1 atm of CO.

2—The range of silica compositions amenable to study was found to be limited at the high silica concentrations by the formation of β silicon carbide and was extended to the liquidus composition in the low silica slags.

3—Lines of constant silica activity, corresponding to constant silicon in the metal, disagree with conclusions of Chang and Derge based on electromotive force measurements.

4—The silicon of the metal increases as alumina replaces lime at a constant percentage of silica. It is also highly dependent on lime:silica ratio.

Acknowledgments

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Attainment of Equilibrium in Gas-Metal Reactions

by Nev A. Gokcen

EQUILIBRIA in the reactions between gases and liquid metals have been the subject of many interesting investigations. The experimental realization of true equilibrium, however, is questionable in certain cases due to the lack of conclusive studies in reaction rates. It will be shown here that a systematic interpretation of rate studies with the analysis of prevailing experimental conditions leads to valuable practical information.

The reactions of particular interest are:

$$H_2(g) + \underline{S}\ (\text{in Fe}) = H_2S(g) \qquad [1]$$

$$H_2(g) + \underline{O}\ (\text{in Fe}) = H_2O(g) \qquad [2]$$

$$2H_2(g) + SiO_2(s) = 2H_2O(g) + \underline{Si}\ (\text{in Fe}) \qquad [3]$$

The usual and perhaps the most convenient method of investigation may be illustrated with reaction 1. A stream of gas mixture consisting of $H_2 + H_2S$ is passed over or bubbled through the liquid metal at constant temperature. The ratio of H_2S/H_2 in the entrant mixture is fixed in each experimental run, and, therefore, the composition of melt varies until the establishment of equilibrium.

The purpose of this paper is to derive a formula expressing the minimum time required for the establishment of equilibrium and to compare the calculated values from such a formula with the available data.

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Equations

Reaction 1 is used for the purpose of illustrating the derivation. Let E represent the equilibrium and X the nonequilibrium sulphur in weight percent at any time t in minutes. For the sake of simplicity, it is first assumed that $E > X$ although the results are of general applicability without restriction. It has been shown by Morris and Williams[1] that within a difference of 1 pct S or less, i.e., $E - X \leqq 1.00$, the value of $K'_1 = P_{H_2S}/P_{H_2} \cdot \underline{S}\%$ is very nearly constant. The maximum ratio of available $P_{H_2S}/P_{H_2} = H_2S/H_2$, from which sulphur can be absorbed by metal, is equal to H_2S/H_2 in equilibrium with E (which equals H_2S/H_2 in the entrant gas), minus H_2S/H_2 in equilibrium with X. Thus:

$$\text{Available } H_2S/H_2 = EK'_1 - XK'_1 \qquad [4]$$

Eq. 4 expresses that sulphur can be absorbed by metal from the H_2S/H_2 in the entrant gas until the gas leaving the metal assumes a value of H_2S/H_2 which is in equilibrium with the dissolved sulphur X at that time.

H_2S constitutes up to approximately 1 pct of the gas mixture. Its disassociation into H_2 and S_2 is about 1 pct at 1600°C, hence, the H_2S/H_2 impinging on the surface of metal is very close to that in the entrant gas. The rate of flow of hydrogen entering the reaction chamber is kept constant experi-

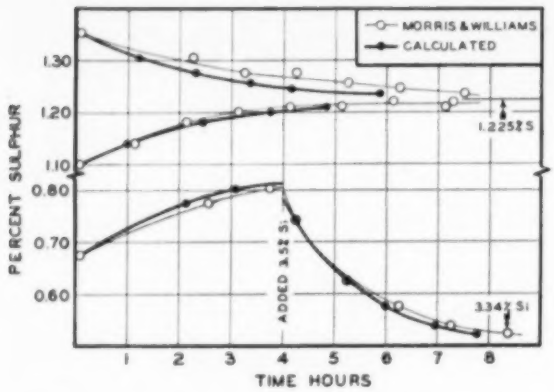

Fig. 1—Reaction rate at 1615°C. Upper curves $H_2S/H_2 = 0.00304$; lower curves $H_2S/H_2 = 0.00220$.

mentally. This is equal to the hydrogen passing through the entire apparatus, because the variation in the amount of hydrogen due to the reaction of part of H_2S with metal is extremely small. Let L represent liters of hydrogen (measured at 0°C and 1 atm) passing through the apparatus. Eq. 4 multiplied by L is equal to the available H_2S in liters per min from which:

$$\text{grams of S available per min} = \frac{32L}{22.4} K'_1(E - X) \quad [5]$$

is obtained.

It should be emphasized that Eq. 5 represents the maximum amount of sulphur that can be absorbed per unit time by the metal containing X pct S at the time t. The minimum time required to reach equilibrium can be calculated by assuming that the maximum rate of sulphur transfer prevails, i.e.:

$$\frac{32L}{22.4} K'_1 (E - X) = \frac{W}{100} \frac{dX}{dt} \quad [6]$$

where W is the weight of metal in grams and dX the infinitesimal change in composition as the result of sulphur transfer. By rearranging Eq. 6 and integrating with $X = X_o$ when $t = 0$, the following general expression is obtained:

$$\log \frac{E - X_o}{E - X} = \frac{62.1 \times L}{W} K'_1 t \quad [7]$$

It is obvious that for $E = X$ the required time is infinity. Theoretically, this is correct but on account of the limitations in experimental methods, the attainment of equilibrium within 95 to 99 pct of the ideal E value is satisfactory and would require a finite or usually limited period of time. Eqs. 4 and 7 are not limited to the condition of $E > X$; they are also applicable in the exact forms above when $E < X$. It is noteworthy that the algebraic values of Eq. 4 and dX/dt are both negative when $E < X$, and then the value of the former represents H_2S absorbable by the entrant gas or simply the available H_2S/H_2 from the metal.

Applications

Morris and Williams[1] and Morris and Buehl[2] investigated reaction 1 very carefully by bubbling mixtures of $H_2S + H_2$ through the liquid iron at a rate of 1050 ml per min measured at room temperature (970 ml at standard temperature and pressure). They studied the rate of approach to equilibrium with melts containing various elements and showed conclusively that the approach to equilibrium is a fairly slow process. During an experimental run, hourly samples of 2 g were taken from the metal, therefore, the weight of melt was constant only between the two successive samples. The weight loss due to splashing was variable, but in general negligibly small for the purpose of these calculations. Table I shows the results based upon their data in the region where the effect of experimental errors in percent sulphur upon Eq. 6 is small; that is, up to $0.98E$ or $0.99E$ in sulphur contents. Their data, substituted in Eq. 7, yield:

$$\log \frac{E - X_o}{E - X} = 3.61 \times 10^3 \frac{K'_1}{W} \theta$$

where $\theta = t/60$.

The results are plotted in Fig. 1 together with the original curves of the investigators. The agreement between the calculated and actual curves is remarkably good and, with the exception of the two upper curves, the difference is equivalent to 0.01 pct S or less, which is within the average analytical accuracy of the results. A better agreement between the two curves for run No. E-39 may be obtained by taking the initial sulphur 0.02 pct higher. The choice of the same initial composition and time for both the calculated and actual curves reflects the errors in the initial analysis upon the succeeding experimental points.

The agreement shows that the bubbling technique provides very nearly the maximum rate of sulphur transfer expressed by Eq. 6. Morris and Buehl[2] actually realized this fact and pointed out that nearly all of the available H_2S reacted with the liquid metal.

Table I. Minimum Time Required for the Change of Composition Toward Equilibrium in the Experiments of Morris and Williams

Run No.	Pct S, X††	Time, Hr: Actual††	Time, Hr: Calculated, θ
E-29	0.684	0.08	0.08
(Equil. $S = 0.86$*)	0.775	2.56	2.11
(Initial $W = 61.35$ g**)	0.801	3.75	3.09
E-29	0.741	4.25	4.25
(Equil. $S = 0.50$*)	0.624	5.25	5.26
($W = 55.65$ g at 4.26 hr)	0.576	6.25	5.98
	0.538	7.25	6.96
	0.521	8.37	7.77
E-39	1.353	0.08	0.08
(Equil. $S = 1.225$†)		1.25	
(Init. $W = 52.1$ g)	1.305	2.25	1.20
	1.275	3.25	2.30
E-44	1.10	0.05	0.05
(Equil. $S = 1.225$)	1.14	1.12	0.98
(Init. $W = 51.65$ g)	1.18	2.12	2.45
	1.20	3.12	3.75

* Equilibrium sulphur is calculated by using $H_2S/H_2 = 0.00220$ and taking $K_o = 0.00256$. After the silicon addition, E is computed by using $0.00256 = K'_1/f_s$ where f_s is the activity coefficient of sulphur. Plotting f_s vs pct S by using the four equilibrium runs in ref. 1, it is found that $f_s = 1.72$, from which $E = 0.50$ pct S whereas a short extrapolation of their curve in Fig. 1 gives a value closer to 0.51 pct S. The choice of $E = 0.51$ would shift the calculated curve in Fig. 1 slightly to the right near the equilibrium sulphur and would make the agreement perfect.

** The weight used in each interval is the previous weight minus 2 g of sample, e.g., $W = 59.35$ from 0.08 to 2.56 hr, and 57.35 from 2.56 to 3.75 hr, etc.

† The mean value between the experimental curves for E-39 and E-44 near equilibrium. See Fig. 1.

†† The values plotted but not tabulated in ref. 1. These, as well as the initial weights, were kindly furnished by J. P. Morris, whose cooperation is gratefully acknowledged.

Run E-39 was made under $H_2S/H_2 = 0.00310$, therefore the reported values of sulphur are corrected to $H_2S/H_2 = 0.00304$ as pointed out by the investigators.

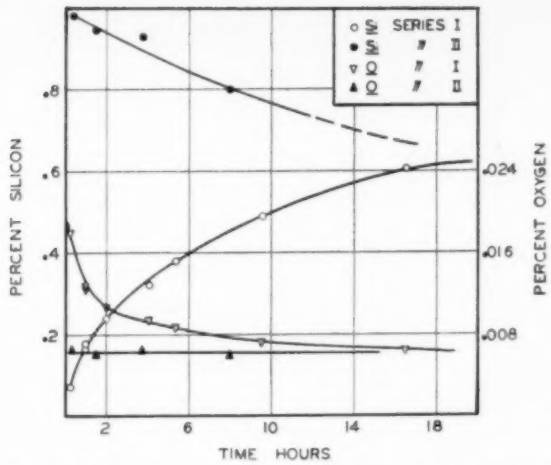

Fig. 2—Reaction rate at 1600°C. H_2O/H_2 = 0.0182, data of Gokcen and Chipman.

The earlier investigation of Chipman and Li[3] on reaction 1 was later superseded by those of Sherman, Elvander, and Chipman,[4] Sherman and Chipman,[5] and Chipman and Sherman,[6] who used 175 g of metallic charge and passed a mixture of $H_2 + H_2S$ over the melt at a rate of 500 ml per min.[4] Table II gives the results of calculations by using in Eq. 7, their values for L, W and K'_1 for each heat in which the only varying dissolved element was sulphur.

In the experimental results of Sherman et al., the initial charge of sulphur, and the time used to obtain equilibrium were not given. It was mentioned, however, that after the melt had been at constant temperature for 1 hr, the first sample was taken and at hourly intervals the metal was sampled and analyzed until the three successive samples yielded identical results and then the melt was " . . . considered . . . " at equilibrium without further proof. The three successive hourly samples limit a period of 2 hr when θ is taken as zero for the first sample. The accuracy of sulphur analysis in their experiments was not given explicitly but it may safely be assumed as ±0.005 pct whereas Morris and Williams reported that their duplicate samples usually checked within 0.01 pct. Accordingly, an actual change of 0.01 pct S in metal may not be indicated by the three samples which appear to yield identical results when the dissolved sulphur is a substantially lower fraction of the equilibrium value as shown in the last column of Table II. Further, in view of the similarity of apparatus used in these and other investigations,[5, 6] it will be shown later in this paper that the calculated minimum time should be multiplied by a factor of two to three in order to obtain a closer magnitude of their actual experimental time. This is quite likely the result of less intimate contact of the gas with metal than that obtained by the bubbling technique. The gas mixture in their experiments was directed over the metal through a preheater tube located at a certain distance above the surface of the melt and, therefore, a part of the gas must have escaped without reaching to and reacting with metal. (See Fig. 1 or ref. 4 for the arrangement of apparatus and compare with Fig. 2 of ref. 9.) Consequently, the experimental results of Sherman et al. are seriously questionable especially in the range of sulphur below 1 pct.

Eqs. 4 to 7 can be modified to make similar calculations on the experiments of Rosenqvist and Cox. The calculations show that the required time could have been decreased proportionally by increasing the rate of gas circulation which was of the order of 60 ml per min in their experiments.

Equilibrium in reaction 2 was recently studied by Dastur and Chipman.[8] The average rate of hydrogen flow was 260 ml per min, the weight of metal 70 g, and the equilibrium constant $K_2 = H_2O/H_2 \cdot \underline{O}\% = 3.93$ at 1600°C in their investigation. The charge, consisting of electrolytic iron, contained initially $X_o = 0.080$ pct O as reported by the manufacturer, and the equilibrium heats less than 0.140 pct. The deviation in their oxygen analyses was usually 0.0006 pct, and occasionally 0.0020. These data cannot be used directly in equations similar to 4 and 7, because in this case L varies substantially with time as $L = 0.260 + W\ 22.4\ dX/100 \times 16\ dt$. Thus Eqs. 4 and 6 assume the following forms for reaction 2:

$$\text{Available } H_2O \text{ in liters per min} = 0.260\,K_2E - LK_2X \qquad [4a]$$

$$\frac{16}{22.4}\left[0.260\,K_2E - K_2X\left(0.260 + 0.98\frac{dX}{dt}\right)\right] = 0.70\frac{dX}{dt} \qquad [6a]$$

Integration and rearrangement of Eq. 6a gives:

$$(1 + K_2E)\log\frac{E - X_o}{E - X} + \frac{K_2}{2.3}(X_o - X) = \frac{16 \times 0.260 \times 100 \times K_2}{2.3 \times 22.4 \times W}t = 0.453t \qquad [8]^*$$

* Eq. 7 is a special form of 8 in view of the fact that $K'_1 \cdot E$ and $K'_1 \cdot (X_o - X)/2.3$ are very small for reaction 1 and may be omitted with an error of less than 1 pct.

Eq. 8 gives the minimum time of 4.8 min for the variation in oxygen content from 0.080 to 0.138 when E is taken as 0.140. If 33 pct of the available oxygen was transferred experimentally into the melt as will be shown later, then 14.6 min should be sufficient to establish equilibrium in this reaction. This is in good agreement with their experimental result showing that the equilibrium was established within approximately 15 min.

The application of the preceding equations to the rate studies of Gokcen and Chipman[9] in reaction 3 is not so simple due to the considerable variation of $K'_3 = (H_2O/H_2)^2\ \underline{Si}\%$ with silicon content and the simultaneous change in oxygen concentration. The variation in dissolved oxygen, however, is small above 0.30 pct Si and it can be estimated from Fig. 2, or calculated by using $[\underline{Si}\%][\underline{O}\%]^2 = 2.8 \times 10^{-3}$; the latter gives a total variation of only 0.0004 pct O for a gain of 0.10 pct Si from 0.45 to 0.55, hence, the effect of $d[\underline{O}\%]/dt$ on the available rate of H_2O is negligibly small in this range. Therefore, equations similar to 4, 5, and 6 may be used to calculate the minimum time for the gain of 0.10 pct Si from 0.45 to 0.55 pct. From their data, $W = 35$ g, $L = 0.260$ liter per min; from a short extrapolation of the lower curve for silicon in Fig. 2, it is found that $E = 0.62$ pct from which $K'_3 = 2.05 \times 10^{-4}$ at equilibrium, and at the average silicon value of 0.50, $K'_3 = 2.12 \times 10^{-4}$. The latter value of K'_3 is found graphically from a curve passing through log 2.05×10^{-4} and 0.62 pct Si, and parallel to the curve of log K'_3 vs pct Si for the equilibrium runs with fully preheated gas mixtures. The choice of K'_3 in this man-

Table II. Minimum Time Required for the Gain of Sulphur Toward Equilibrium in the Experiments of Sherman Et Al.

Run No.	$K'_1 \times 10^3$	E	Sulphur, Pct** Initial X_o	Sulphur, Pct** Final X	Minimum Time, Hr, θ†	Equivalent Time, Morris et al.‡	S Pct = x' When Gain = 0.01 Pct S Per 2 Hr	$\frac{x'}{E} \times 100$ Pct
S-23*	2.02	4.21	4.00	4.04	4.33	0.64	4.104	97.5
M-1	2.18	2.11	1.985	2.025	7.27	1.07	2.011	95.3
M-4	2.27	1.25	1.16	1.20	10.5	1.54	1.155	92.4
M-17	2.20	0.67	0.603	0.643	17.0	2.50	0.572	85.4
M-27	1.976	0.42	0.363	0.403	25.2	3.71	0.312	74.3
M-36	1.56	0.25	0.20	0.24	42.0	6.18	0.114	45.6
F-3	2.835	0.312††	0.259	0.299	20.7	3.04	0.235	75.3

* Runs S-23 and F-3 are from refs. 4 and 6 respectively; others are from ref. 5.

** X/E 100 pct = 96 pct and $X - X_o$ = 0.04 pct S. The substitution of these values in Eq. 7 gives log $(1 + 1/E) = 10.64K'_1\theta$. X_o/E 100 pct is 90, 86, and 80 pct for runs M-17, M-27, and M-36, respectively.

† For X/E 100 pct = 96 pct and $X - X_o$ = 0.08 pct S, the time required for the heats of M series is 12.5, 17.2, 25.7, 36.2, and 57.5 hr, respectively.

†† The highest sulphur reported in ref. 6. (See also ref. 5.)

‡ Calculated by using the data in cols. 2 to 4 and the experimental conditions of Morris et al.[1,2] θ of Sherman et al. divided by θ of Morris et al. equals approximately 6.8 for the same E, X, and X_o values.

ner, for the runs in reaction rates, is due to the existence of thermal diffusion as the result of insufficient preheating of the entrant gas as pointed out by the investigators. The equation for the maximum rate of silicon gain is then:

$$\frac{d[\text{Si}\%]}{dt} = \left(\sqrt{\frac{2.12 \times 10^{-4}}{\text{Si}\%}} - 0.0182\right)\frac{0.260 \times 14}{0.35 \times 22.4} \quad [9]$$

The calculation from the integrated form of this equation shows that the increase of silicon from 0.45 to 0.55 should require 1.58 hr, whereas the experimental time is 4.8 hr. The effective fraction of the available oxygen is then 1.58/4.8 or 33 pct, which increases somewhat with increasing silicon. The graphical solution is obtained by determining at 0.50 pct of average silicon, (a) the slope $d[\text{Si}\%]/dt$ from Fig. 2, and (b) the maximum slope $d[\text{Si}\%]/dt$ directly from Eq. 9; the ratio of (a) to (b) is the effective fraction which is 32 to 36 pct depending upon the graphical accuracy of the slope.

Conclusions

Eq. 6 shows explicitly that for a given reaction, W should be small, L large, and X_o as close to E as possible in order to decrease the time required for the attainment of a final concentration near the equilibrium value. In a series of similar reactions, with the same values of W, L, X_o/E, and X/E, approach to equilibrium is faster for higher values of K (cf. reactions 1 and 2).

It may be pointed out that Eq. 6 is sufficiently accurate for most purposes involving high temperature investigations. The exact form is:

$$\frac{dX}{dt} = AK(a_E - a_X) \quad [10]$$

where A is the combined constants for a reaction of the type 1 or 2 together with the experimental conditions, K is the true equilibrium constant, and a the activity based upon percent concentration, i.e., $a_X = f_X \cdot X$. Substitution of the activity coefficients in Eq. 11 as:

$$\frac{dX}{dt} = \frac{AK'_E}{f_E}(f_E \cdot E - f_X \cdot X) =$$

$$AK'_E\left(E - \frac{f_X}{f_E}X\right) \quad [11]$$

shows that Eqs. 6 and 11 are identical when f_X/f_E is unity, which is very nearly the case when the initial value of $E - X$ is small. In exceptional cases, such as in reaction 2, $K'_2 = K_2$, hence f_X/f_E is unity. Experimental results are seldom accurate enough to give a ratio of f_X/f_E as a function of X for the integration of Eq. 11. A comprehensive use and discussion of this equation will be in a forthcoming paper together with new data.

The reactions above are being studied by using a cascade-type platinum wound furnace, and by following the technique of Morris and coworkers with some improvements in view of the foregoing considerations regarding the reaction rates.

Summary

The equation $\log \frac{E - X_o}{E - X} = \frac{62.1 \times L}{W} K'_1$ is derived to relate the time required (t) to the change of percentage of sulphur in liquid iron from (X_o) towards (X) in the direction of the equilibrium sulphur (E) in the reaction:

$$H_2\,(g) + \underline{S} = H_2S\,(g),\ K'_1 = \frac{H_2S}{H} \cdot \frac{1}{\underline{S}\%}$$

The constants L and W represent the hydrogen flow rate and the weight of metal respectively.

Similar equations are derived for the reactions:

$$H_2\,(g) + \underline{O} = H_2O\,(g)$$

$$2H_2\,(g) + SiO_2\,(s) = \underline{Si} + 2H_2O\,(g)$$

Available data and experimental methods are analyzed, interpreted, and critically evaluated by using the derived equations.

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Technical Note

Lattice Parameter of Beta Titanium at Room Temperature

by B. W. Levinger

THE lattice parameter of the β form of pure titanium has been measured at elevated temperature.[1, 2] No attempt was made, however, to correct the parameter obtained to room temperature.

In the course of phase diagram studies at Armour Research Foundation and elsewhere, the variation of β-phase lattice parameter with composition has been established in a number of binary and ternary systems involving titanium. It was possible to extrapolate in these instances to 100 pct Ti to find the apparent lattice parameter of β titanium at room temperature. Table I lists the results thus obtained. The suggested value for the lattice parameter of β titanium is the average of the extrapolated values 3.276 $\pm$0.003 kX. This suggested value gives an interatomic distance in β titanium of 2.837 kX and hence a Goldschmidt atomic diameter (coordination number 12) of 2.925 kX. The latter agrees closely with the value of 2.93 given by Hume-Rothery.[3]

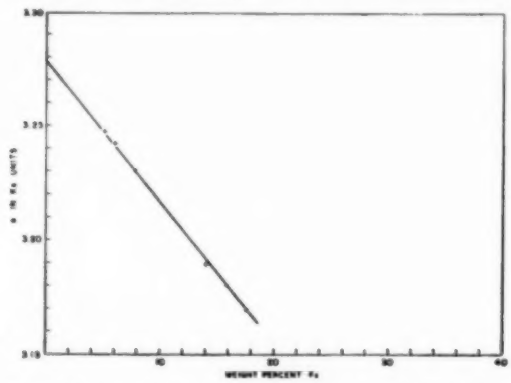

Fig. 1—Lattice parameter vs composition of β phase in binary Ti-Fe alloys.

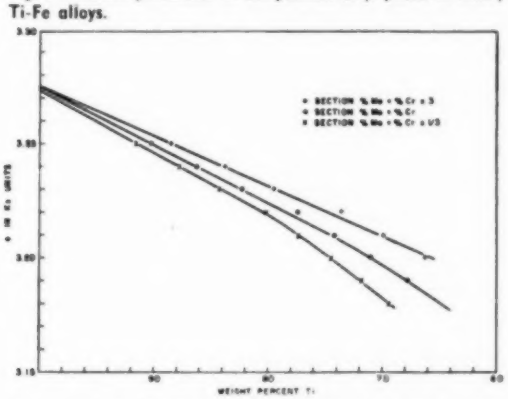

Fig. 2—Lattice parameter vs composition of β phase in ternary Ti-Mo-Cr alloys.

From the data of Adenstedt and coworkers[4] it was possible to determine by extrapolation the mean coefficient of linear expansion for β titanium in the range from room temperature to 1000°C. This value, 10.1×10^{-6} per degree C, compares with about 11×10^{-6} for α titanium in a similar range.[5] It was thus possible to calculate the parameter at 900°C. The value of 3.305 kX agrees well with 3.3065 given by Eppelsheimer.[6]

Table I. Apparent Lattice Parameter of Beta Titanium at Room Temperature

System	Extrapolated β Phase Parameter (kX)	Limit of Stable β Phase Wt Pct Ti	Reference
Ti-V	3.275	85	4
	3.28	85	6
Ti-Cr	3.278	94	7
Ti-Mo	3.276	90	8
Ti-Nb	3.276	64	8
Ti-Fe	3.278	96	9 Fig. 1
Ti-Mo-Cr	3.275		9 Fig. 2
Ti-Mo-Mn	3.277		9 Fig. 3

The majority of values reported in the literature[1-4, 8] were given as Angstroms. In at least one case, ref. 8, it was shown that they actually represented kX units. The source of this confusion appears to be that a large number of tables of X-ray emission spectra list wavelengths as Angstroms and give values in kX units. The accepted conversion factor for kX units to Angstroms (10^{-8} cm) is 1.00202. Thus the parameter of β titanium suggested corresponds to 3.282A.

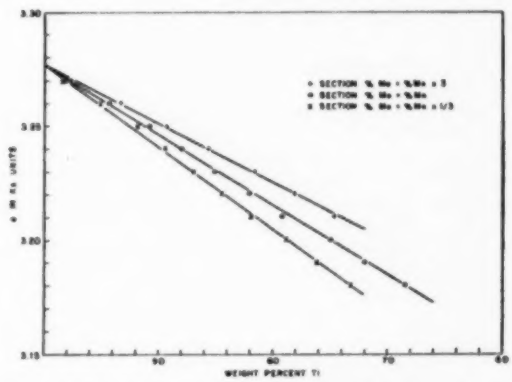

Fig. 3—Lattice parameter vs composition of β phase in ternary Ti-Mo-Mn alloys.

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Technical Note

High Temperature Modification of $TiCr_2$

by B. W. Levinger

THE system Ti-Cr has been studied by several investigators.[1-4] Though titanium and chromium are completely miscible at high temperatures, an intermediate phase of the approximate atomic proportions $TiCr_2$ has been identified at various compositions between 60 and 68 wt pct Cr. The structure of this phase was established as the cubic C15 ($MgCu_2$) type with 24 atoms per unit cell and a lattice parameter 6.929 kX.[3]

During a study of the ternary system, Ti-Mo-Cr,[5] the existence of a high temperature modification of the $TiCr_2$ phase was discovered. In a series of alloys annealed at 1300°C and containing from 60 to 70 wt pct Cr and 5 pct Mo, a new phase was present which did not correspond to either β solid solution or $TiCr_2$. By trial, the new phase was identified to be of the hexagonal C14 ($MgZn_2$) structure with 12 atoms per unit cell. Further work showed that the hexagonal structure was, in fact, also present in binary Ti-Cr alloys quenched from high temperatures.

To make the identification more certain, the intensities of the various reflections were calculated assuming a composition $TiCr_2$ and C14 structure. Table I lists reflection planes, interplanar distances, calculated intensities, and a comparison of these values with the lines of a binary Ti-Cr alloy (66 pct Cr) annealed for 20 min at 1385°C and water quenched. Since high angle lines were more diffuse, the correspondence between visually observed and calculated intensities was not as good at these angles.

Lattice parameters were computed to be a = 4.922 kX, c = 7.945, c/a = 1.614. The corresponding interatomic distances are: titanium to titanium distance, 3.00, kX, chromium to chromium distance, 2.43, kX, titanium to chromium distance, 2.88, kX. These compare to 3.00, 2.45, and 2.87 kX in the cubic phase, respectively.[6]

The atomic positions in the C14 structure are as follows:

Titanium 1/3, 2/3, z; 1/3, 2/3, ½-z;
2/3, 1/3, $\bar{z}$; 2/3, 1/3, ($\bar{\frac{1}{2}}$-$\bar{z}$);

Chromium 0, 0, 0; 0, 0, ½;
$2x$, x, ¼; $\bar{2x}$, $\bar{x}$, ¾;
$\bar{x}$, $\bar{2x}$, ¼; x, $2x$, ¾;
$\bar{x}$, x, ¼; x, $\bar{x}$, ¾;

The values of x and z were calculated for the alloy mentioned and found as follows: $z = 0.061, x = 0.165$. The values assumed in the intensity calculations were those for an ideal close-packed lattice or z = 1/16, x = 1/6.

Work in the Ti-Mo-Cr system indicates that γ_2, the hexagonal modification of $TiCr_2$, is the stable phase above 1300°C, while γ_1 with the cubic structure is stable below 1000°C. X-ray examination of a number of alloys annealed at intermediate temperatures showed that the hexagonal and cubic phases can coexist. Alloys quenched from 1000°C and annealed at 1100° and 1200°C showed small amounts of γ_2 at the higher temperature. A considerable amount of γ_2 seemed present, however, in cast alloys annealed at 1100°C. It further appears that there is a small but definite solubility range for both phases in the ternary system.

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Table I. Diffraction Data for $TiCr_2$ (γ_2 Phase)

hkl	d, Calculated* (kX)	d, Observed† (kX)	Intensity Observed‡	Relative Intensity Calculated§	Corresponding Data for γ_1 d (kX)	Corresponding Data for γ_1 hkl
110	2.461	2.454	w	0.14	2.44	220
103	2.250	2.247	wm	0.36		
200	2.131	2.127	vft	0.05		
112	2.092	2.087	m	0.57	2.08	311
201	2.058	2.056	m	0.54		
004	1.986	1.985	w	0.13	1.99	222
202	1.878	1.876	w	0.13		
104	1.800	1.798	vw	0.07	1.73	400
203	1.660	1.657	ft	0.04		
210	1.611	1.610	vft	0.01	1.59	331
300	1.421	1.419	vft	0.02	1.411	422
213	1.376	1.377	wm	0.15		
302	1.338	1.337	wm	0.14	1.333	511
006	1.317	1.323	vft	0.02		
205	1.274	1.272	wm	0.23		
214	1.251	1.251	vw	0.06		
220	1.230	1.229	wm	0.21	1.223	440
206	1.125	1.124	w	0.17	1.167	531
107	1.097	1.095	vft	0.04	1.094	620
313	1.079	1.078	w	0.17		
401	1.056	1.055	vw	0.17	1.057	533
224	1.046	1.045	w	0.27	1.045	622
402	1.029	1.029	vft	0.06		
314	1.016	1.015	ft	0.08		
207	1.002	1.001	vft	0.07	0.9976	444
108	0.9672	0.9686	ft	0.10	0.9708	711
410	0.9301	0.9285	ft	0.06	0.9255	642
217	0.9279			0.08		
323	0.9173	0.9171	vw	0.21		
412	0.9056	0.9052	wm	0.19	0.9021	731
226	0.9014			0.21		
405	0.8850	0.8851	w	0.37	0.8662	800
218	0.8454	0.8453	w	0.34		
406	0.8302	0.8306	vw	0.37		
317	0.8187	0.8186	ft	0.15	0.8168	822
308	0.8139	0.8138	ft	0.13		
332	0.8033	0.8035	w	0.53		
421	0.8014	0.8013	wm	1.00	0.8003	555
0010	0.7945	0.7950	vft	0.11	0.7946	662
422	0.7894	0.7894	vw	0.48		
504	0.7834	0.7837	ft	0.20		
407	0.7769	0.7769	vft	0.61	0.7746	840

* d observed from an alloy containing 66 pct Cr-34 pct Ti water quenched from 1385°C.

† d calculated from lattice parameters: a = 4.922 kX, c = 7.945. These lattice parameters were obtained by the method of least squares from eight lines of the above pattern.

‡ Observed Intensity: m, medium; wm, weak medium; w, weak; vw, very weak; ft, faint; vft, very faint. In a number of cases, lines were diffuse and it was felt that they represented a pair of lines. This is indicated by bracketing.

§ Relative Calculated Intensity: The values of relative intensity for planes from (110) to (220) are due to Wallbaum.[6] Actually they represent corresponding values for the isomorphous phase, $TiMn_2$; calculation of a number of lines at higher angles showed that the two values correspond within a few percentage points.

Acknowledgment

The results of this paper represent work carried out in conjunction with a project sponsored by Watertown Arsenal, Contract No. DA-11-022-ORD-272.

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Arc-Furnace Equipment and Its Operation At the Kennecott Utah Refinery

by H. A. Shaw and H. G. G. Whitton

This paper describes the use of the electric-arc furnace for the production of tough-pitch, horizontal cast copper shapes and the production of copper anodes from tank house anode scrap. This installation is the only one of its kind in the United States.

SINCE the initial use of electric-arc furnaces for refined copper melting on a commercial scale at Copper Cliff in 1936, this type of melting has been of extreme interest to everyone in any way connected with copper casting and fabricating. Early in 1948, Kennecott Copper Corp. decided to build an electrolytic copper refinery at Garfield, Utah. One of the major decisions to be made at that time was the type of furnace to be used for melting cathodes for casting into refined copper shapes and for melting anode scrap for the production of anodes. Based on the results obtained from arc furnaces by the International Nickel Co. of Canada, at Copper Cliff, and by the American Smelting and Refining Co., at Baltimore, coupled with certain important economic factors such as having an adequate amount of relatively cheap power available at the Magna Central Power Plant, high cost of poles and oil in the Salt Lake District, and the lack of natural gas at that time, the final decision was to install electric-arc furnaces rather than the standard type of reverberatory furnaces.

Experience has shown certain parts of the original installation to have been inadequate or in need of modification. Although the present status of arc-furnace melting at the Utah Refinery is far from perfect, nevertheless substantial progress has been made.

At the Utah refinery, copper is melted in three 15-ft diam, size "M" Lectromelt furnaces, two of which are used for melting cathodes and one for remelting anode scrap.

Each furnace is energized from a 13,800-225 v, 3-phase, 60-cycle, 6000-kva (at 40°C rise) oil-immersed water-cooled transformer. Auxiliary equipment for each refined copper furnace includes a charging machine, launders, ladle, 40 ft diam Walker-type casting wheel, bosh, and inspection conveyor. The anode furnace differs in that it is charged by hand from an elevated platform and the anodes are picked off the 24-ft diam casting wheel by a takeoff hoist and loaded directly into specially designed trailers, Figs. 1 and 2.

Electrical Equipment

Electric power to operate the arc furnaces is generated at the Kennecott-owned Magna Central Power Station two miles distant and transmitted to the Refinery outdoor substation at 44,000 v. At this point it is stepped down to 13,800 v and carried through concrete-lined underground tunnels to the switchgear and then to the primary side of the furnace transformers. The power is conducted from the Y-connected secondary bus bars of the transformer to the electrode arms by means of 22 flexible copper cable conductors per phase. Each cable has a cross-sectional area of 1,750,000 circular mils, giving a total area of 38,500,000 circular mils per phase. The power is carried from these cables to the three individual electrode holders by means of water-cooled copper bus tubing. The electrode clamps are incorporated in the electrode holders and are released by air pressure working against a spring in the clamp control cylinder.

The movement of the electrode arms is either automatic or manual. The automatic control is used during melting and is regulated by three Westing-

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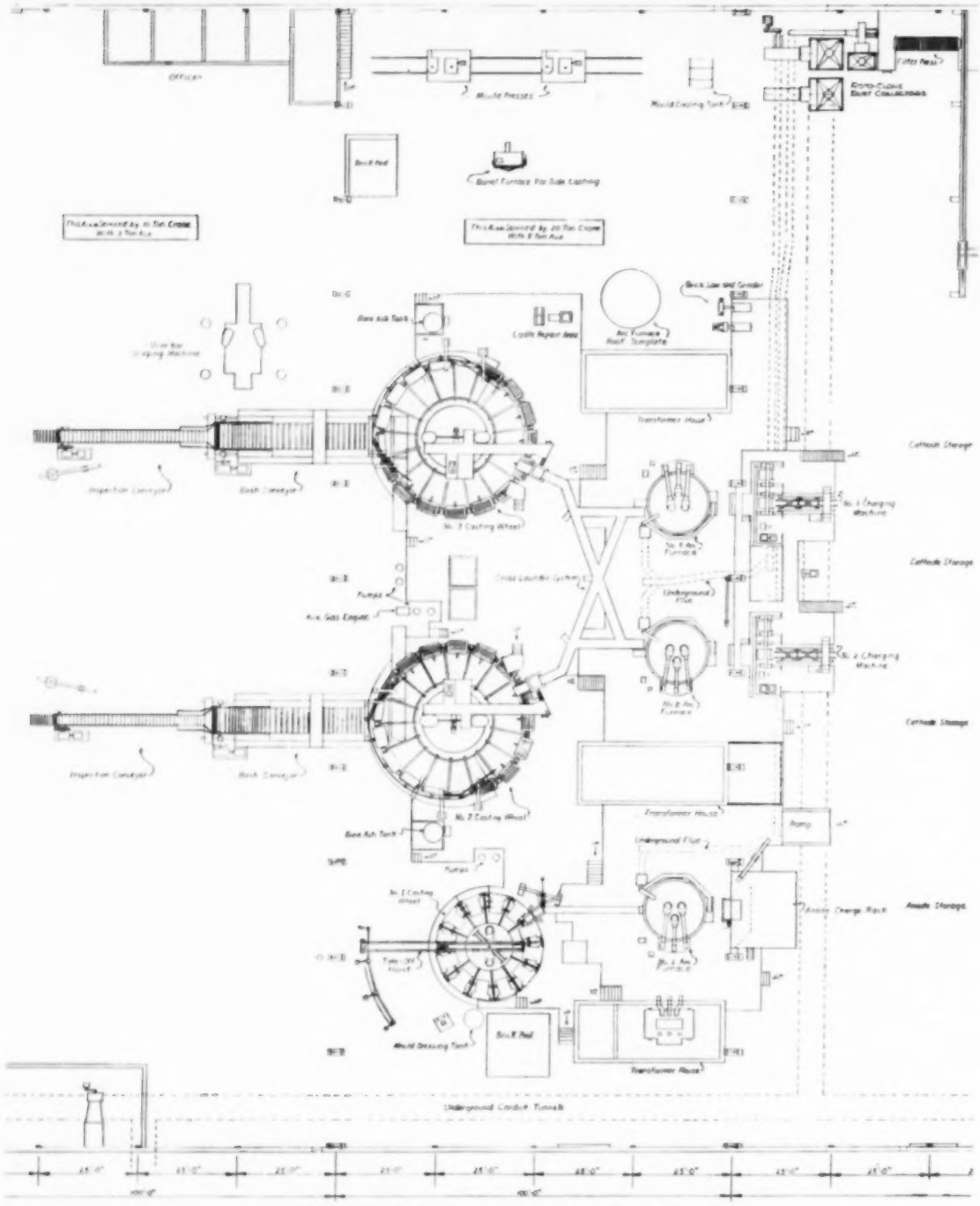

Fig. 1—Diagrammatic layout of furnaces and casting equipment.

house Rototrols which actuate the electrode arm winch motors. The manual control is used whenever it is necessary to raise one or all the electrode arms, such as prior to shutting off the power, or slipping electrodes. The low voltage connections in the transformer provide 13 taps ranging from 85 to 225 v. Suitable connections may be made to a motor operated tap changer which allow the operator to use any one of four selected voltages. Present settings give a selection of 120, 147, 173, or 190 v phase to phase. Most melting is done using 173 v. A rheostat on each phase provides a limited control of the current for each tap setting.

Data compiled during the two years of operation indicate that 245 kw-hr of power are required to melt one ton of copper.

Description of Furnaces

The three arc furnaces are identical in construction. The walls are fabricated of 1⅛ in. steel plate, cylindrical in form, having an inside diameter of 15 ft 0 in., and provided with four openings, namely,

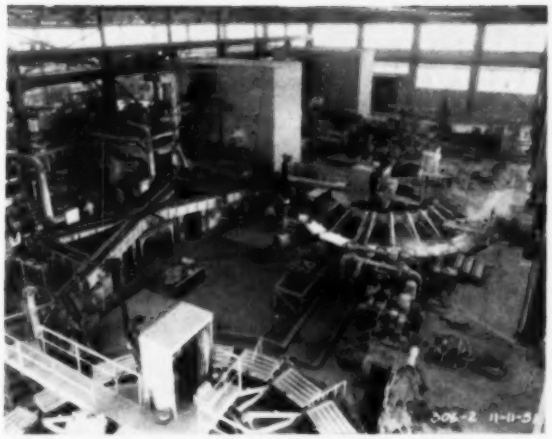

Fig. 2—General view showing the two refined copper melting furnaces and auxiliary casting equipment in the foreground. The anode copper melting furnace and casting equipment is in the background.

charge slot, skim bay, taphole, and a small inspection hole near the taphole. The charge slot is located at the rear of the furnace diametrically opposite the furnace taphole. The skim bay is on the side opposite the masts, 45° from the charge slot. The furnace bottom is also made of 1⅛ in. steel plate formed on a 14 ft 2 in. spherical radius. For pouring the furnaces are hydraulically tilted about an axis in line with the furnace taphole spout.

The holding capacity of the furnaces when new is approximately 50 tons. The wear on the bottom refractories resulting from operations increases this quantity to about 65 tons before relining of the bottom is necessary.

Furnace Refractory Construction

The furnace lining consists of a refractory cement pad 1 to 8 in. thick formed on the bottom of the empty shell to develop the desired radius for the construction of the superimposed brick bottom. This is followed by two courses of 2½ in. brick keys laid to conform to the desired spherical radius. The third course is constructed from 9 in. special shape, chemically bonded magnesite brick, and the fourth and final course is built from 13½ in. special shape, chemically bonded magnesite brick. The main section of the side walls is built from 9x6x3 in. No. 1 keys laid up as headers and backed up by two 4½ in. courses of fireclay brick. An anti-surge ledge projects 9 in. at the metal line. Special precautions are taken to allow vertical expansion to take place without exerting pressure on the roof brick. An annular space between the bottom brick and the sides of the steel shell is allowed. This space is filled either with insulation brick or powdered magnesite to permit expansion of the bottom. Expansion is also provided in the side walls above the metal line by the use of ⅛ in. corrugated paper between each brick, Fig. 3.

Only basic brick will withstand the corrosive action of the furnace atmosphere due to the concentration of copper oxide fume at high temperature. This fume will react rapidly with silica brick, high alumina brick, and to a lesser extent with refractories of a sillimanite or mullite composition. Silicon carbide brick will withstand the action of the fumes but rapidly breaks down to a silica slag in the presence of oxygen at elevated temperatures that are at times unavoidable.

As low refractory costs and avoidance of operational shutdowns are two of the major objectives of arc-furnace melting, it is necessary that every detail of furnace construction be carefully engineered and that the refractories be selected with due regard to previous results. The actual taphole consists of a 4 in. ID carbofrax tube set in place with magnesite cement in a slot left during the construction of the wall. Accurate location of this tube is important because it determines the level of the molten copper in the furnace, acts as a skimmer, and because it must be positioned so that the furnace can be drained completely. When casting must be interrupted it is only necessary to tilt the furnace back 5° onto safety blocks. This allows the molten copper to drain from the inclined taphole tube. It is possible to hold a furnace full of molten copper in this position for an indefinite period by intermittent application of power.

Arc-Furnace Roof Construction

Roofs are constructed with basic brick using 9x 4½x3 in. series of brick plus some special shapes. When building a roof, the fabricated steel roof support ring is located accurately about a permanent cement template, the surface of which is a dome having a spherical radius of 17 ft 4 in. Wooden templates are set by dowels so that the electrode and vent openings will be located accurately in the finished roof. The roof is developed by constructing a series of brick rings using side arch and wedges to follow the shape of the cement template. Rings of specially shaped, adapter brick are used as needed. The electrode and vent openings are made by using special side arch wedge shapes that form a slightly conical opening with the larger diameter up so that the brick rings are held in position by a definite taper. Circumferential expansion is allowed by the use of a ⅛ in. corrugated cardboard spacer every eighth brick. At the present time no cement is used in laying the brick. However, after the roof has been installed on the furnace and the temperature raised, the outside surface of the roof is grouted with a thin slurry of magnesite cement to seal the openings between adjacent brick, Fig. 4.

The desirability of roof insulation is being investigated and its use will depend upon results obtained from current experiments.

Since the melting practice requires definite control of the furnace atmosphere, it is necessary that

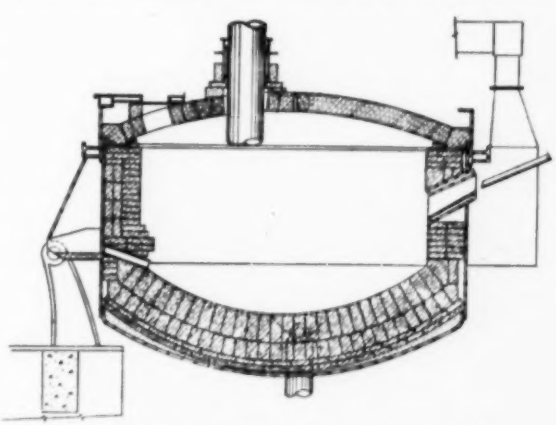

Fig. 3—Section of arc furnace showing arrangement of refractory lining. Diagrammatic section of roof shows section through vent, electrode opening and main portion of roof.

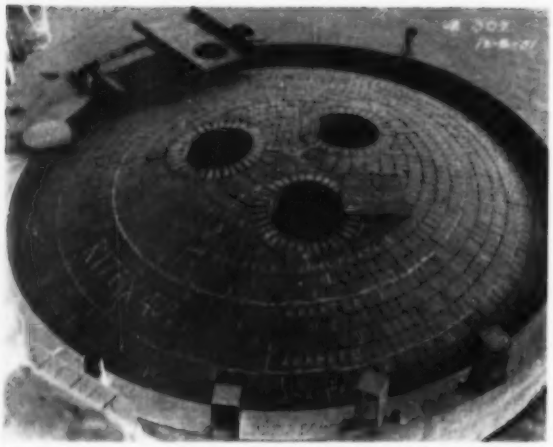

Fig. 4—Arc furnace roof for 18 in. diameter electrodes, showing water-cooled vent plate and water-cooled banjo-type damper.

a gas-tight seal be provided around the electrodes, otherwise "bottlenecking" of the electrode will occur and gas will escape from the furnace. Individual water-cooled glands are used on each electrode. These glands are suspended several inches above the furnace roof. A flat ring of fireclay key brick is set on the roof around each electrode opening so that the small end of the brick comes in contact with the graphite electrode, thus protecting the lower face of the water-cooled electrode gland from copper splash. With a new cold roof, a space of 2 in. is allowed between the lower face of the gland and the fireclay brick pad. This allows the roof to rise due to the expansion of the brick while being brought up to operating temperature, without subjecting the roof to the additional weight of the glands. This opening is sealed by forming a slip joint using a soldier course of fireclay side arch brick strapped to the gland and projecting down so as to come in contact with the fireclay base. The weight of the water-cooled gland is carried from the operating platform by projecting lugs from each gland. These are electrically insulated from the steelwork of the platform by fireclay brick. The glands now in service are fabricated from $\frac{3}{8}$ in. boiler plate. The roof vent opening is built from

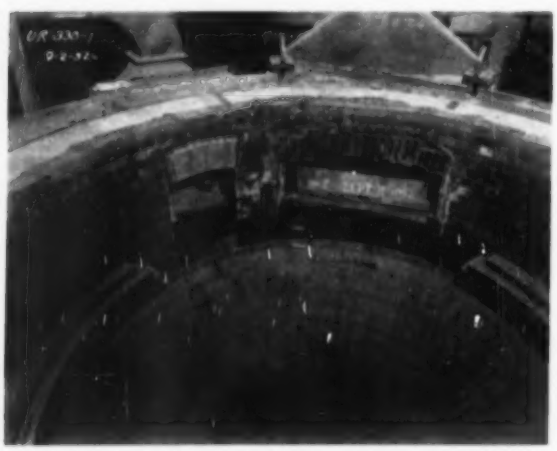

Fig. 5—Refractory lining in refined copper arc furnace showing new brick bottom, anti-surge ledge and water-cooled, boiler plate charge slot.

9x6x3 in. side arch wedge brick to form a slightly conical opening 13 in. in diameter. A water-cooled base plate, constructed from $\frac{3}{4}$ in. boiler plate and containing a 13 in. diam opening, is cantilevered over the vent in such a manner as to allow the weight of the water-cooled section to be carried by the steel roof ring without interfering with the expansion of the roof.

Charge Slot Construction

The original construction of the wirebar furnace charge slot followed previous practice which consisted of a water-cooled copper casting bolted to the outside shell of the furnace and having a minimum opening 44 in. wide x $4\frac{1}{2}$ in. high. The original anode furnace charge slot was similar in design to the standard, copper, water-cooled charge slot casting, but was fabricated from $\frac{3}{4}$ in. boiler plate. The minimum opening was 59 in. wide x 6 in. high, making it possible to charge anode scrap or rejected, full sized anodes. On the outside, a steel door operated by an air cylinder was installed. The refractory portion of the chute consisted of a sill built from special shapes of silicon carbide designed to give a slope of 30°. Trouble was experienced from the start with this construction. The silicon carbide sill brick had a very short life, the extreme heat seriously warped the steel door, and the continual spray of molten metal rapidly formed an objectionable build up of copper skulls on the refractory adjacent to the water-cooled opening of the slot. It was felt that these troubles must be associated with the use of higher arc voltages inherently necessary with 60 cycle power, as such troubles were not encountered on a similar installation using lower voltage and 25 cycle power. As will be discussed later, it was also felt that the 14 in. diam electrodes being used were too small.

It then became necessary to develop a new charge slot construction to meet these conditions. After exhausting the practicabilities of various refractories it was decided to investigate the possibility of using a water-cooled boiler plate slot. In April 1951, a water-cooled boiler plate sill was installed and results were very promising. Development of the idea was continued until at the present time each furnace is equipped with a complete water-cooled charge slot consisting of the sill, two side sections, and a top section. As a safety measure the charge slots have been raised approximately 10 in. to avoid the possibility of the water-cooled section coming in contact with molten copper when the furnace is set back on the low blocks at such times when it may be necessary to stop casting, Fig. 5.

Electrodes

The original furnace installation utilized 14 in. diam graphite electrodes. Shortly after operations started it was realized that the 14 in. diam electrodes would not give the desired melting rate. In spite of every effort it was not possible to obtain melting rates above 15 tons per hour. To obtain this value it was necessary to operate on the higher voltage positions which in turn caused the furnace walls and roof to overheat dangerously to the point of destruction. In an effort to correct this a change was made to 18 in. diam electrodes.

At the time it was reasoned that the larger diameter electrodes would tend to shield the arc to the extent that the sidewalls would not overheat as much, thus making it possible to operate for longer

periods of time on the higher voltage positions. It was also thought that the percentage of down time due to broken electrodes would be decreased because of the greater mechanical strength of the larger electrodes. Experience has proved this reasoning to be correct. Results of the change from 14 to 18 in. diam electrodes are summarized as follows: 1—Melting rate was increased from 15 to 22 tons per hour. 2—Lower wall temperatures enabled the furnace to operate on higher voltages without too much danger of overheating. 3—Less electrode breakage resulted in a decrease in electrode consumption from 5.0 to 4.2 lb per ton. 4—Power factor decrease from 0.7 to 0.6 resulted in greater load on transformer. 5—Stability of the arc at the same current value decreased.

Efforts made to increase the power factor at the furnace by changing the current, voltage, or reactance have not proved successful. While it has been possible to increase the power factor by lowering the current, this has in turn given rise to increased arc instability. Likewise, raising the voltage beyond 173 v, phase to phase, gives rise to overheating and instability.

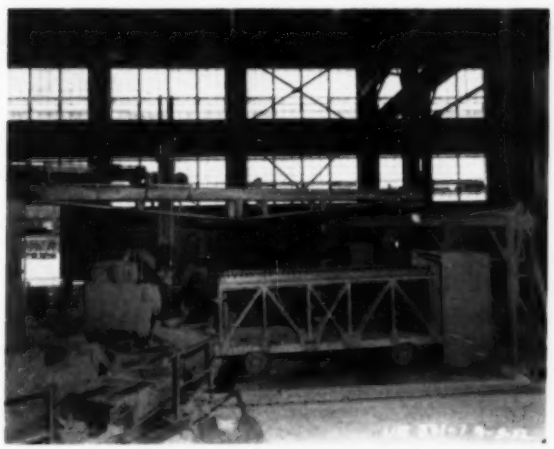

Fig. 6—Anode take-off hoist and cooling sprays used to cool anodes and remove scale after anodes are placed in anode rack cars.

Anode Copper Furnace

As previously mentioned the construction of the anode furnace is identical to the two refined copper furnaces except for a wider charge slot. In contrast to the refined copper furnaces, the anode furnace is hand charged from an elevated platform.

As in the refined furnaces the copper flows from the furnace taphole down the launder into the pouring ladle and is then cast into one of the 12 molds on the 24 ft diam casting wheel. After cooling, the tops of the anodes are raised approximately 2 in. by push-up pins so that the take-off hoist can pick them up and hang them, properly spaced on an anode trailer. Adequate water cooling is provided by overhead sprays through which the loaded trailer is moved so that the anodes will be cooled and some of the scale removed by quenching before they are delivered to the tank house, Fig. 6.

Launders, Ladle, and Wheel

Molten copper from the cathode melting furnace flows from the furnace taphole into launders arranged so that it is possible to cast into either or both of the two wheel positions. The copper flows from the launders directly into a pouring ladle and then is cast into one of the 17 molds on the 40 ft diam Walker-type casting wheel. The casting wheel revolves continuously with the wire bars being dumped into a water bosh located diametrically opposite the ladle position. After dumping, the molds are automatically righted and then hand sprayed with a slurry of bone ash and water. The refined shapes fall on a steel conveyor in the bosh where they are cooled and then elevated to a second conveyor for inspection and loading.

Fig. 7—Arc furnace showing fume recovery system.

The original plant construction included a vertical-type, low frequency induction furnace unit at each casting wheel, so arranged that the molten copper could flow down the launder from the arc-furnace taphole and enter the induction furnace through a 5 ft refractory tube set in the hollow trunnion about which the induction furnace was rotated.

Starting February 4, 1951 experiments were conducted in casting molten copper direct from the arc-furnace launder into the pouring ladle. It was found that by close pyrometer control of casting temperature, rate of charging, and condition of the copper at the taphole that casting conditions could be

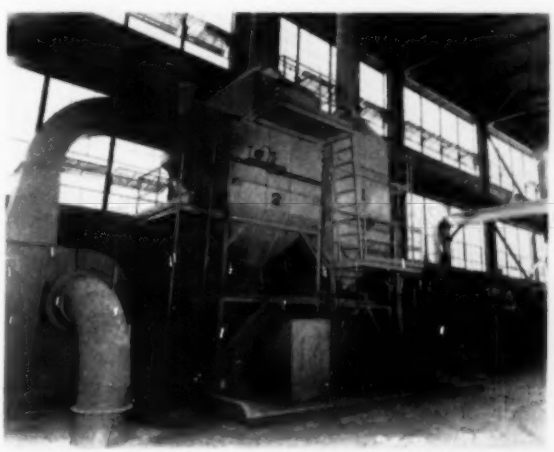

Fig. 8—Fume oxide recovery system, showing suction fan, two Roto-Clone units. One of the three filter press units is shown mounted over a fume oxide storage bin.

Fig. 9—Charging machine illustrating method of charging cathodes and reject wirebars into the arc furnaces.

maintained more uniformly and casting delays almost entirely avoided with the elimination of the induction units.

Fume Recovery System

The fume recovery system is divided into two parts: one is used to collect the fume oxide from the anode furnace and the other is used to collect the fume oxide from the two refined copper furnaces. This is to keep the anode fume, which must be re-treated to remove the impurities and precious metal values, separate from the relatively pure copper oxide dust recovered from the refined copper furnaces.

The fume that escapes through the roof vent contains from 5 to 6 lb of cuprous oxide for each ton of copper melted. The charge slot skim door and vent are adequately hooded and are connected to a central fume pipe, Fig. 7. The fume is forced through a type N, Roto-Clone collector, the exhaust gases pass through a 25 in. diam stainless steel stack 45 ft high. The slurry containing the copper oxide dust is pumped through a 36 in. filter press, Fig. 8.

Charging

As no refining is accomplished in the usual operation of the arc furnace, every effort is made to insure that the cathodes used for melting are free from nodulation, have a fine grained structure, and are washed to completely remove electrolyte. Special attention is given to washing electrolyte from the pockets formed by the cathode loops. The washed cathodes are stacked directly from the tank house washing machine on to rubber-tired, four wheel, steered trailers. Each trailer carries two piles of cathodes having a total average weight of 15,000 lb. After weighing, the stacks of cathodes are removed from the trailers by use of fork lift trucks and stored in an area directly behind the arc furnaces. Each of the two refined copper furnaces has an independent charging machine, consisting of a structural steel framework which supports a carriage containing two hydraulic tilting magazines, Fig. 9. Each magazine is designed to take a full pile of cathodes. The carriage is operated electrically so that when a charged magazine is lined up with the furnace charge chute a pair of hydraulically operated rams enables the operator to push the slightly inclined cathodes into the charge chute at any desired rate. The charging rate is determined by the furnaceman who takes into consideration the casting rate desired, the pouring temperature, and the average weight of the cathodes being charged. The furnaceman sets the desired charging rate on the dial of a flexopulse, this causes a light to flash at the charging operators stand each time a cathode should be charged. In the meantime a pile of cathodes is being lifted and placed into the empty magazine of the charging machine by means of a 10-ton, overhead crane. As soon as the companion magazine is empty, the carriage is moved over allowing the newly filled magazine to come into charging position.

Cathodes from the charging machine slide down an inclined chute, through the water-cooled charge slot, directly into the bath of molten metal. Reject wirebars are charged back into the furnace by means of a chute that extends from the operating platform of the cathode charging machine to the charge slot.

Furnace Operation

The furnace operating crew consists of a furnaceman for each operating furnace, two chargers for each wirebar furnace, and three chargers for the anode furnace. One overhead craneman services the charging aisle and the crane follower hooks up the charge material for each operating furnace and records the necessary information regarding amount of material charged.

The set and oxygen content of the cast shapes is controlled by regulating the flow of gas and fume through the 13 in. diam water-cooled vent in the roof. A banjo shaped water-cooled boiler plate damper is used to regulate the vent opening. When the vent is closed the reducing action of the volatilized carbon from the electrode arc and the volatilized copper from the superheated copper at the point of arc impingement causes rapid reduction of the oxygen content of the molten copper. When the vent is opened the scavenging action of air which enters at the charge slot removes these elements and allows the molten copper to pick up oxygen. Control of the set of the cast copper shapes is maintained by careful regulation of the vent opening. Spot optical oxygen determinations are made every half-hour on samples taken at the furnace taphole along with block samples taken at the point where the molten copper flows from the furnace taphole into the launder leading to the pouring ladle. In normal operation the furnace is held in a horizontal position, the molten copper flowing from the furnace due to displacement by the incoming cathodes. The tilting mechanism enables the operator to tilt the furnace forward 45° when it is necessary to drain it, or tilt it backward 5° when skimming or during holdovers.

In all arc furnaces used for melting copper the arc strikes on a comparatively bare bath of molten metal. Melting under this condition results in a characteristic wave motion in the molten metal which in turn gives rise to excessive short circuit current surges. Meter readings become wild, sidewall temperatures rise, melting rate decreases and the furnace transformer tends to overheat. To overcome this characteristic a refractory ledge has been built at the metal line and extending in toward the center of the furnace approximately 9 in. This, however, is only a partial cure and it is necessary to cause a refractory slag ledge or shelf to build up and extend in still further to act as a damper to the wave motion. Since there are normally no slag making constituents available in the furnace, except ash from the consumed electrode, it is necessary

to cover part of the bath with magnesite material containing the desired amount of lime and silica. The arc fuses this material to a viscous condition and as the fluid or semifluid slag is formed the action of the arc showers it on to the walls of the furnace. Eventually it flows down the side of the wall and strikes the refractory ledge and extends in over the bath of molten metal, and as the metal temperature is lower than the wall temperature a ledge of slag develops around the metal line of the furnace except at the charge slot and skim bay sections. It has been observed that the melting rate of the furnace increases up to a certain point, as the ledge increases. Any of the brick that spalls from the walls or roof eventually causes the bank or ledge to grow until at times the build up may extend beyond an electrode. An opening may or may not develop which will allow the arc flame to come in contact with the molten bath. In such cases it is necessary to stop casting, open up the skim bay door and break off and remove the excess portion of ledge.

The amount of regular skimming necessary is entirely dependent upon the amount of refractory material that accumulates and is mostly caused by refractory failure. Under normal conditions the so-called slag consists of porous lumps of material, impregnated with small masses of copper. Ideal melting conditions are usually possible only after a good shelf has formed and the surface of the bath partly covered by the so-called slag. It is of extreme importance that the bath should not be allowed to become fully covered so that arcing will occur on the covering of the bath. If this happens a new set of conditions then immediately develops, the meters become stabilized, there is no surging in the low tension leads, the usual crackling noise that is an indication that copper melting is progressing in a satisfactory manner ceases and is replaced by a strong characteristic hum. At the same time copious fumes of volatilized carbon issue from the vent in the roof, and wall and shell temperatures rise at an exceedingly high rate, which in a very short time can cause destruction of the roof and wall above the metal line. Simultaneously the copper temperature will drop due to the insulating covering on the bath. If the operator attempts to raise the metal temperature by increasing the power input then destruction of the furnace will progress at a still more rapid rate. Under these conditions the copper rapidly becomes oxygen free and is then fouled by the presence of undesirable elements. It will be observed when this happens that the molten copper flowing from the taphole no longer has a bright metallic appearance, but is soon covered by a dull flaky scum.

During the charge slot cleaning operation, also when slipping and adding electrodes, it is of course necessary to shut off the arc power and tilt the furnace forward to provide molten copper for the continuation of casting. Due to these delays an actual furnace melting rate of 22 tons per hour will only result in a continued casting rate of 19 to 20 tons per hour. Tercod pouring lips on the casting ladles enable casting to be continued 24 hr a day for as long as four days, without a shut down. Upon the completion of the tonnage requirements for a certain cast shape, the copper is diverted to the appropriate launder and casting is commenced on the alternate wheel which has previously been loaded with molds for casting the desired shape.

At the present time only horizontal shapes of electrocopper are cast at the Kennecott Utah Refinery, however, the melting equipment is ideal for the production of all types of vertical cast electro and deoxidized shapes if these should be required at some future date.

Acknowledgment

The writers wish to express their appreciation for the considerable time and help in the preparation of this article extended by Stanley Hughes, Assistant to the General Manager of Western Operations for Kennecott, and the entire Casting Department Staff of the Kennecott Utah Refinery, particularly that of M. C. Edlund.

Technical Note

Effect of Carbon on the Volume Fractions and Lattice Parameters Of Retained Austenite and Martensite

by C. S. Roberts

THE advent of a sensitive X-ray method of analysis recently has allowed the determination of retained austenite in amounts as low as 0.3 pct.[1] As a result this phase has been found in quenched low carbon steels where its presence has not been generally suspected.

In the course of a study of the tempering process,[2] retained austenite determinations were made by the X-ray method on a series of high purity Fe-C alloys and plain carbon steels. The chemical analyses of these materials and details of the hardening procedure are given in Table I. Results were obtained after quenching to 72°F (22°C) and −321°F (−196°C). Austenitizing temperatures were between 100° and 150°F above A_3 or A_{cm}. All proeutectoid cementite or ferrite was in solution. The combination of the results with those of Averbach, Castleman, and Cohen,[1] and earlier results of Esser

C. S. ROBERTS, Junior Member AIME, is associated with Metallurgical Laboratories, The Dow Chemical Co., Midland, Mich.

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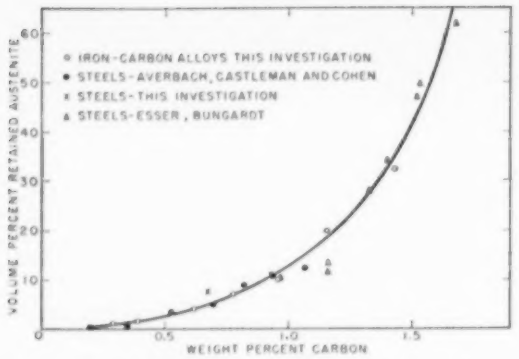

Fig. 1—Effect of carbon content on retained austenite content after quenching to room temperature.

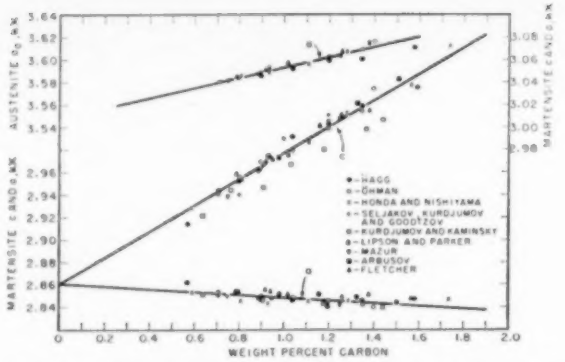

Fig. 3—Variation of martensite and austenite lattice parameters with carbon content.

and Bungardt[3] are shown in Figs. 1 and 2. The results are better-defined functions of carbon content than have been available previously. The variation is smooth and there is no significant difference between the behavior of the high purity alloys and the plain carbon steels.

Also necessary for this work was a collection of all known data showing the effect of carbon content

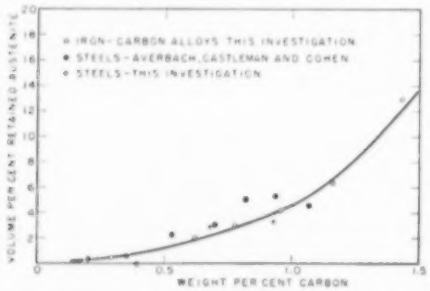

Fig. 2—Effect of carbon content on retained austenite after refrigeration to −321°F (−196°C).

on the austenite and martensite lattice parameters. All of the results which could be found[4-12] are shown in Fig. 3. The data of Kurdjumov and Kaminsky are apparently low. Neglecting their points, the parameters in kX units may be expressed by the function: Martensite: $c = 2.861 + 0.116x$; $a = 2.861 - 0.013x$; $c/a = 1.000 + 0.045x$; and austenite: $a = 3.548 + 0.044x$; x = wt pct C.

Acknowledgment

The author is grateful to S. G. Lorris, who performed the X-ray determinations and to B. L. Averbach and M. Cohen for guidance of the work.

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Table I. Composition and Metallography of Alloys

Alloy or Steel No.	C, Pct	Mn, Pct	Si, Pct	Austenitizing Temperature, °F	Quenching Medium	Fracture Grain Size	Retained Austenite, Quenched to 72°F, Pct	Retained Austenite, Refrigerated, Pct
122	0.29	*	*	1600	10% brine	6	1.2	0.4
123	0.39	*	*	1550	10% brine	5	1.6	0.1
124	0.62	*	*	1500	10% brine	4½	4.1	2.0
103†	0.68	0.78	0.21	1500	Water	6	7.6	2.9
125	0.78	*	*	1500	10% brine	5½	7.0	3.0
105†	0.93	0.42	0.19	1550	Water	6	11.0	3.3
126	0.96	*	*	1550	10% brine	4½	10.0	4.1
127	1.16	*	*	1650	Water	70%1, 30%>1	19.9	6.4
128	1.43	*	*	1850	Water	>1	32.3	12.9

* For the high purity alloys, silicon and oxygen <0.01 pct, all other elements <0.001 pct.
† Steel.

AIME OFFICERS:

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Vice-Presidents—O. B. J. Fraser, J. L. Gillson, Philip Kraft, James B. Morrow, L. F. Reinartz, R. W. Thomas
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aime NEWS

Metals Branch Bylaw Revisions to Be Voted On During Annual Meeting in February

Suggested bylaw changes of the various divisions of the Metals Branch to be adopted during the Annual Meeting, February 1953 are given below. They will be voted upon during the respective division meetings. Deletions for the Institute of Metals Div. and Iron and Steel Div. are in parenthesis and additions are in italics. Revisions for the Extractive Metallurgy Div. are given in one paragraph.

Institute of Metals Div.

Article I

Name and Object

Sec. 2. The object of the Division shall be to furnish a medium of cooperation between those interested in the *field of physical metallurgy; that is* (metallurgy) *the nature, structure, alloying,* fabrication, *heat treatment, properties* and uses of (the nonferrous) metals (and their alloys); to represent the AIME insofar as (nonferrous) *physical* metallurgy is concerned, within the rights given in AIME Bylaw *Article* XI, Sec. 1. and not inconsistent with the Constitution and Bylaws of the AIME; to hold meetings for (social intercourse and) the discussion of (nonferrous) *physical* metallurgy; to stimulate the writing, *publication,* presentation and discussion of papers of high quality on (nonferrous) *physical* metallurgy; to *accept or* reject (or accept such) papers for presentation before meetings of the Division.

Article IV

Meetings

Sec. 3. At (any) *a* meeting of the Division, for which notice has been sent to the members of the Division through the regular mail *or by publication in the* JOURNAL OF METALS at least one month in advance, a business meeting may be convened by order of the Executive Committee and any routine business transacted not inconsistent with these Bylaws or with the Constitution or Bylaws of the AIME.

Article V

Officers and Government

Sec. 1. The officers of the Division shall consist of a Chairman, a Senior Vice-Chairman, *a* (one) Vice-Chairman, *a* Secretary and *a* Treasurer. The Office of Secretary and Treasurer may be combined in one person, if desired by the Executive Committee.

Article VI

Committees

Sec. 1. There shall be (six) standing committees as follows: (Papers and Programs Committee,) *Programs Committee,* Finance Committee, Membership Committee, Annual Lecture Committee, *Technical Publications Committee, Mathewson Gold Medal Committee, Nominating Committee,* (Data Sheet Committee,) (and Annual Award Committee) *Education Committee* and such other Committees as the Executive Committee may authorize.

Sec. 2. It shall be the duty of the (Papers and) Programs Committee to secure the presentation of papers of appropriate character at meetings of the Division (and of the AIME).

Sec. 6. *It shall be the duty of the Technical Publications Committee to appraise manuscripts of technical papers of subject matter within the scope of the Division that may be submitted to the AIME for publication in the Transactions; to recommend their acceptance, revision or rejection.*

Sec. 7. *It shall be the duty of the Mathewson Gold Medal Committee to recommend the author[s] of a paper published in the Transactions Section of the* JOURNAL OF METALS *as recipient[s] of this Medal in accordance with conditions stipulated by the Executive Committee.*

(Sec. 9. Appointments on standing committees shall be for terms of three years with approximately one third of the committee membership being appointed each year.)

Sec. 9 It shall be the duty of the Education Committee to assist in the accreditation of metallurgical curricula through the Engineers' Council for Professional Development and such other duties related to the education of prospective metallurgical engineers as shall be referred to it by the Executive Committee.

Article VII

Nomination and Election of Officers and Executive Committee

(Sec. 2. A Nominating Committee of five members of the Division shall be appointed by the Chairman of the Division subject to the approval of the Executive Committee.)

Sec. 2. *In addition to the nominations made by the Nominating Committee [see Article VI, Sec. 8,]* any ten members of the Division may submit nominations for one or more offices to the Executive Committee not later than August 15, and the persons so nominated shall be included in the official ballot.

Sec. 3. The voting shall be by letter ballot, except *that* when only one candidate has been nominated for each elective position by August 15 following publication of the Nominating Committee report in the July issue of (Mining and Metallurgy) *the* JOURNAL OF METALS [or thirty days after publication in a subsequent issue], no letter ballot shall be sent to the membership and the candidates shall be declared elected at a subsequent meeting of the Board of Directors of AIME.

Article VIII

Amendments

Sec. 1. Proposals to amend these Bylaws shall be made in writing to the Executive Committee and signed by at least ten members. They shall be considered by the Executive Committee and announced to the members through the columns of (Mining and Metallurgy) JOURNAL OF METALS, together with any comments or amendments made by the Executive Committee thereon. They shall be voted upon at the annual

meeting of the Division in February or by letter ballot, as may be directed by the Executive Committee.

Iron and Steel Div.

Article I

Name and Objects

Sec. 2. The objects shall be to furnish a medium of cooperation between those interested in the metallurgy and industry of iron and steel manufacture (and use) to represent the AIME in so far as ferrous *production* metallurgy is concerned, within the rights given by AIME Bylaw XVII, Sec. 3, and not inconsistent with the Constitution and Bylaws of the AIME; to hold meetings for (social intercourse and) the discussion of ferrous *production* metallurgy; to stimulate the writing, presentation and discussion of papers of high quality on ferrous *production* metallurgy; to reject or accept such papers for presentation before meetings of the Division.

Article V

Officers and Government

In Sec. 3 add Chairman of the Membership Committee as an ex-officio member of the Executive Committee.

In Sec. 4 amend to read each member except ex-officio member of the Executive Committee shall serve for 3 years.

Article VI

Committees

(Sec. 3. The Committee on Papers and Programs shall consist of the Chairman of the Division and of the Chairman of the standing technical committees and of such other committees of the Division as the Executive Committee may designate.)

Article VII

Nominations and Election of Officers and Committees

Sec. 5. The voting shall be by letter ballot, except that when only one candidate has been nominated for each elective position by August 15 following publication of the Nominating Committee report in the July issue of JOURNAL OF METALS (Mining and Metallurgy) *or thirty days after publication in a subsequent issue,* no letter ballot shall be sent to the membership and the candidates shall be declared elected at a subsequent meeting of the Board of Directors of AIME.

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Extractive Metallurgy Div.

Article I, Sec. 2, line 6, (social intercourse and.)

Article V, Sec. 2, line 2, (in-so-far.) Sec. 5, substitute Terms of office for officers and Executive Committee members shall begin and end at the close of Annual Meetings.

Article VI, Sec. 1, line 4, *or discharge committees* before when. Line 5, (necessary) *desirable.*

Article VI, Sec. 2, line 2, (the) *for* and (first of.) Sec. 3, line 4, put a period after papers near the end of the line and delete the balance of this section.

Article VII, Sec. 3, *to take office at the close of the Annual Meeting* at the end. Sec. 5, line 2, (officers to) *offices of.* Sec. 9, delete.

Attendance at AIME Annual Meeting Urged

Last month we made a plea for a more liberal attitude by company executives on allowing their staff to go to professional meetings, specifically the AIME Annual Meeting. We pointed out the advantage to the company thereby to be gained. Younger men, particularly, need to be sent to technical meetings. They will come back better equipped to do the job they have been hired to do, and also more enthusiastic about their job—a better friend of the company.

One reason we have been given why a company executive may be disinclined to send staff members, particularly the younger ones, to a meeting is that they thereby have better opportunities to get other jobs, and hence the company loses them. This is a selfish attitude, of course. If a man seeks another job it is usually because he is dissatisfied where he is, and if that is the case he will leave sooner or later anyway unless the company removes the causes of his dissatisfaction. If a man is loyal to his employer, happy in his work and merely succumbs to a better offer from some one else, no self-respecting employer should stand in the way of his advancement. He might ask himself if that is not the way he, too, got ahead in the profession.

A few go to large meetings and come back with memories of a good time but no particular addition to their store of gray matter. Their time has been largely wasted, as has that of their employer. Admittedly it takes a bit of experience to get the most out of an AIME Annual Meeting, but even the first trip can be rewarding. We strongly urge a bit of collateral reading—a short article that appeared in the first issue of this journal, that of January 1949. It was written by E. H. Rose, and was entitled, *Getting Your Money's Worth.* Look it up before you leave for Los Angeles, or the next meeting that you attend. **E. H. Robie.**

To Hold Second Northwest Conference

The Second Pacific Northwest Metals & Minerals Conference will be held in Seattle, Wash., on Thursday, Friday, and Saturday, May 14 to 16, 1953. All events will be held at the Benjamin Franklin Hotel. Plant visits will be held Thursday afternoon, technical sessions on Friday and Saturday, and the climax will be a banquet on Saturday evening. A series of events will also be planned by the WAAIME. General Chairman for the Conference is G. A. Waterman, with J. G. Johnston as Metals Chairman, and Sheldon Glover as Industrial Minerals Chairman.

The Iron & Steel Div. session will cover electric furnace operations. Emphasis will be on various relatively new or novel procedures that have resulted in improved quality, reduction in melting time, or reduction in material cost.

Extractive Metallurgy Div. will present a series of interesting papers including one on *Modern Safety Methods in Nonferrous Smelters.*

A number of interesting papers reporting on recent research problems in physical metallurgy will be presented in Institute of Metals Div. sessions.

The trend toward scientific education in metallurgy will be the primary consideration of the Engineering Education session. Views of men engaged in mineral dressing, research, light metals production, and teaching will be presented.

The Industrial Minerals groups will have two sessions covering a wide range of subjects. Included will be the topics *Industrial Steam,* and *Natural Gas,* which are of special interest at this time.

Changes Made In Nominating Committee

The following changes in the personnel of the Nominating Committee for AIME Officers in 1954 were made by the Executive and Finance Committees: Robert H. Ramsey in place of Francis Cameron as alternate, representing the New York Section. J. A. Morris as representative of the East Texas Section. Mr. Ramsey's address is care of *Engineering and Mining Journal,* 330 W. 42d St., New York 18, N. Y., and Mr. Morris' is P. O. Box 312, Kilgore, Texas.

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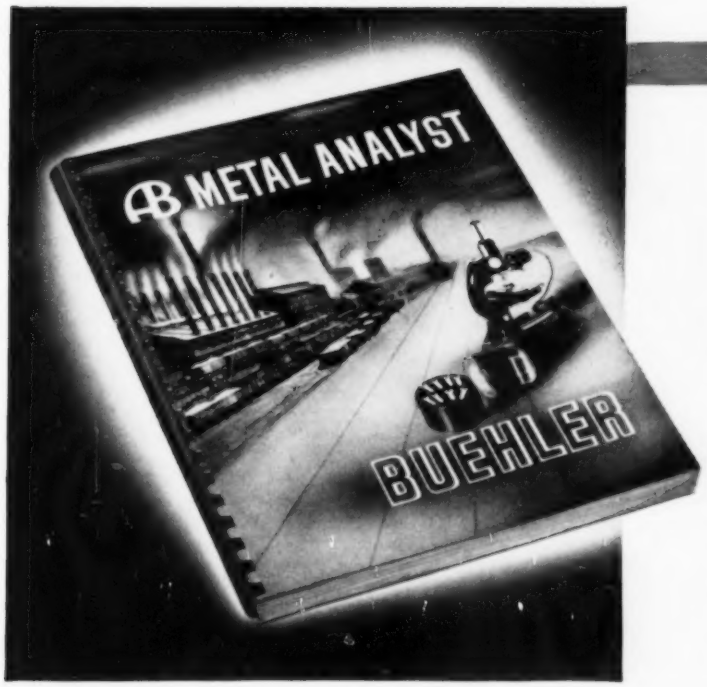

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ANDREW FLETCHER

President, AIME, 1953

ANDREW (Drew) FLETCHER is a fighter. He brings to the Presidency of the AIME a record of having gone all the way with every project he has ever undertaken. Drew Fletcher stays with whatever he undertakes until the task is completed to his satisfaction. More than that, he is a man of conviction, who stands by his beliefs with a surety that only a complete grasp of the situation involved can give. But there is still more to the man who will guide the destiny of the AIME during the coming year.

Sitting in his office at 250 Park Ave., where he performs his tasks as president of St. Joseph Lead Co., one sees a simply furnished room, unadorned for the most part, and designed for working—perhaps because the man who occupies it has no time for trappings and furbishings which do not contribute to getting the job done. It is the office of a man who takes a direct line to where he wishes to go and to what he wishes done. Yet, it takes only a short time to know that Andrew Fletcher is a man of diverse interests who can talk easily and knowledgeably of many things.

The statistics are simple. Andrew Fletcher was born February 6, 1895, in New York City. He knew ships and shipbuilding before most youngsters are able to climb a ladder without falling.

"My father and grandfather were shipyard owners, here and in Scotland, and I knew that I would go into the business, too."

Before going to work, however, Mr. Fletcher went to the Hill School in Pennsylvania and then to the Sheffield Scientific School at Yale, where he graduated with a Ph.B. in mechanical engineering. But the Fletcher Shipyard in Hoboken, N. J. was still some distance away, as was St. Joe.

"I reasoned that the best way to start was to go to work for someone outside my family. That way, my father would never find out how little I really knew when I finished school. When I went to work at the Fletcher Shipyards, I wanted to be able to hold my own."

Mr. Fletcher went to work as a mechanic for Harlan & Hollingsworth, Wilmington, Del., shipyard. Mr. Fletcher remembers it as a hard school, with lessons well learned. Memories of ships and the building of them remain in the few pictures that adorn the walls of his office. Photographs of some of America's famous ships are hung about the room.

He takes a deep pride in the fact that once almost all the river boats on the Hudson River were built by his family. But it has been many years since Andrew Fletcher said goodbye to shipbuilding. Before he left, however, he held the position of foreman of the Baltimore Drydock Co., Baltimore, and later as a member of his family's firm, secretary of the Fletcher Shipyard. Toward the end of his shipbuilding career, he was in complete charge of the yard. Today, he maintains contact with ships and shipbuilding through a directorship of the American-Hawaiian Steamship Co. and by association with officials of Bethlehem Steel Co. who now own the old Fletcher yard.

A trustee of St. Joseph Lead Co., since 1921, Mr. Fletcher joined the firm as vice-president and treasurer in 1929. He has been a mining man with the same devotion that previously he gave to ships. He foresees a healthy, steadily expanding American mining industry, providing that the basic truths of the American way of life once again dominate the thinking of the country.

"The United States has forged ahead of other nations because of its underlying philosophies, rather than the more obvious, immediate palliatives which arise, run out their span, and then are forgotten under the innate strength of old established American principles."

Not all the frontiers of the country have been explored, Mr. Fletcher feels.

"Great latent possibilities remain. However, if mining is to grow, the youth of America must be assured of a prosperous mining industry. It can be the job of the AIME to present this prospect."

Mr. Fletcher predicts that the coming year will be a good one for the Institute. He feels, however, that in the past, a single man, in a single year of office, has been asked to do too much. Each of the nine AIME Presidents that he has seen, with only one year of office, was greatly handicapped. The present arrangement, which allows the Past President, the incumbent, and President-Elect to work together is a great step forward, he said.

The Industrial Hygiene Foundation of America in particular and the American Mining Congress stand as examples of improvements accomplished as a result of his association. Each organization is in a substantially better position today than when he found it.

Mr. Fletcher feels that the mining industry in general is faced with a crucial decision. It must shake off the vast network of government control which has descended upon it.

Words once spoken by Thomas Jefferson, and repeated by the president of St. Joe, may be a key to the path Mr. Fletcher's thinking follows on the place of government in the lives of men:

'If we can prevent the Government from wasting the labor of the people under the pretense of caring for them, they will be happy.'

The advice he gives to the young men he talks to is simple. "Our parents took their chances when they came to U. S. and by and large, they prospered. Our job today is to make sure the door of opportunity is held open, so that we can use our training and talents to better ourselves and our fellow men."

Mr. Fletcher has little time or patience with the so-called *liberals* who advocate compulsion in the name of progress and the better life.

"Men are more important than machines and the individual and his personality are the important things in any society which hopes to advance."

Although he has served the AIME in many ways, this is the second office he will hold as an Institute member. Mr. Fletcher was named Treasurer of the Institute upon the death of Harry Hamilton in 1944. He has change of pace, the ability to throw a hard fastball and then what baseball calls the change-up—a good thing for any man to have. To the individual in every day life, it means the ability to live fully. Among the honors Mr. Fletcher has received in recognition of his accomplishments is a doctorate from the Missouri School of Mines in June, 1949.

Aside from business, Mr. Fletcher is active in community and home, holding office as a trustee of the First Presbyterian Church, and as a member of the Planning Board of Mendham, N. J. He is modest about his golf game, but coaxing will bring forth the information that he plays in the eighties. But in late years, golf has suffered because of Mr. Fletcher's home, Three Fields—which occupies much of his free time.

His abiding interest, however, is the American worker, the man who makes the country possible—the man who makes it grow with each passing day.

Personals

James S. Kirkpatrick has been elected president of the Magnesium Assn. Mr. Kirkpatrick is director of research and development for Brooks & Perkins, Inc., Detroit.

S. K. Derderian was appointed assistant general manager of Metal Hydrides, Inc., Beverly, Mass.

A. S. Contrini has resigned as smelter superintendent for Mazapil Copper Co., Mexico and is now metallurgical superintendent for the Cia. Minera de Huehuetenango, Guatemala.

John Poast has been appointed superintendent of the newly established blast furnace dept. at the East Works plant of Armco Steel Corp., Middletown, Ohio. Mr. Poast joined Armco in 1926. In 1946 he was successively appointed assistant to the superintendent and assistant superintendent of the Hamilton blast furnace dept. He became superintendent of that department in 1948. **Edwin A. Keresmer** succeeds him as superintendent of the Hamilton blast furnace dept.

John L. Ham was recently appointed project manager in the metallurgical dept. of the National Research Corp., Cambridge, Mass. Prior to his joining National Research, Mr. Ham was with the Raytheon Mfg. Co. He also has been associated with the Allegheny Steel Co., Jones & Laughlin Steel Co., and Climax Molybdenum Co.

David I. Dilworth, Jr. has been named assistant director of metallurgy for the Crucible Steel Co. of America. He moves to this newly created post from the Sanderson-Halcomb works, Syracuse, N. Y., where he had been chief metallurgist.

George F. A. Stutz, N. J. Zinc Co., Palmerton, Pa., has been transferred to the New York office as development engineer. **David L. Gamble** succeeds Mr. Stutz as manager of research. **Robert K. Waring** has been made assistant manager of research.

J. V. Emmons was elected to the board of directors of the Cleveland Twist Drill Co. Mr. Emmons has been with the firm for 43 years.

Charles P. Miller is associated with the Foote Mineral Co., research and development div., Berwyn, Pa.

Louis Allis, Jr., formerly vice-president in charge of sales, has been elected a vice-president of the Louis Allis Co. **C. G. Skidmore,** formerly sales manager, was elected an officer of the firm as vice-president in charge of sales. He will also be general sales manager.

C. ALLEN, JR.

A. F. FRANZ

C. R. TYSON

Charles Allen, Jr. was named chairman of the board of the John A. Roebling's Sons Corp., a newly-formed and wholly-owned subsidiary of Colorado Fuel & Iron Corp. **A. F. Franz** has been named president and **Charles Roebling Tyson,** executive vice-president.

Harry W. Poole has been appointed director of quality control by Superior Tube Co., Norristown, Pa. He had formerly been associated with the Brown Instrument Div. of Minneapolis-Honeywell Regulator Co.

F. P. Strieter, former chief of the casting section of Dow Chemical Co.'s metallurgical laboratories, has been named assistant superintendent of the die casting dept. Prior to joining Dow in 1942, Mr. Strieter had been with the Chase Brass & Copper Co., Waterbury, Conn.

William Rathbun has become a metallurgist for the General Electric Co., Richland, Wash.

Richard L. Hoff has been appointed development metallurgist for the Superior Tube Co., Norristown, Pa. He was formerly at the Naval Air Experimental Station, Philadelphia.

John J. Lennon, manager of scrap purchases, the American Metal Co., Ltd., has been promoted to assistant manager of the American Metal Co., Ltd. of Illinois.

Van H. Leichliter has been named vice-president of operations, American Steel & Wire. He had been assistant vice-president of operations since 1950.

Ralph N. Fitzpatrick has been appointed district manager of the Cleveland office of Electro Metallurgical Co.

Floyd L. Greene, chairman of the board, General Refractories Co., Philadelphia, has been elected to the board of directors of the First National Bank of Philadelphia.

George Breyer, formerly chief metallurgist for Crucible Steel Co., Midland works, has been appointed metallurgical service engineer for the Detroit area. Mr. Breyer joined Crucible in 1935. He has been contact metallurgist and assistant chief metallurgist, respectively.

Hubert O. Woods is with Allis-Chalmers Mfg. Co., Milwaukee as an erection engineer.

Robert F. Stoops has joined the advance development section, Carboloy Dept., General Electric Co., Detroit. **Anthony D. Cortese** has joined the design and application section, and **Frank B. Nuelle** has been transferred to Detroit from the Schenectady operation.

C. L. Heater, vice-president, American Steel Foundries, Chicago, will head the newly formed transportation equipment div. **R. D. Brizzolara,** vice-president, who is in charge of the Elmes and King Div. will also head the Hammond Div.

A. R. MERZ

A. H. ENGELHARDT

A. Russell Merz and **Allen H. Engelhardt** have been appointed vice-presidents of Cerro de Pasco Corp. Mr. Merz will assume charge of the company's sales and purchases in New York. Mr. Engelhardt will continue to manage the firm's metal mining, smelting, and refining operations at La Oroya, Peru.

Gilbert Soler, formerly in the research and development dept., U. S. Steel Co., has joined Universal-Cyclops Corp., Bridgeville, Pa., as assistant technical director. He has held positions with Timken Roller Bearing Co., and Atlas Steels, Ltd.

William F. Taylor has been appointed manager of structural sections div., Penn Metal Co., Parkersburg, Pa.

George McMeans has been appointed vice-president in charge of operations, Kaiser Steel Corp., Oakland, Calif.

Fred R. Fielding was appointed chief engineer, Buffalo district steel plant, Republic Steel Corp.

H. T. McIlwain was named manager, stone and slag div., Bethlehem Steel Co. He succeeds **John P. Peacock,** who has retired.

Weston G. Thomas has been elected a vice-president of the Climax Molybdenum Co. He is also a director and treasurer of the company.

W. G. THOMAS

John A. Sienker has been named assistant vice-president of operations, American Steel & Wire Div., U. S. Steel, Cleveland. He had been district manager of operations at Duluth.

Richard A. Young is with the American Zinc Lead & Smelting Co., St. Louis. He had been with the American Zinc Co. of Illinois at Dumas, Texas.

George A. Sofer has joined the staff of the National Research Corp. as project manager in the applied physics dept., Cambridge.

Harold Cope, general superintendent of American Steel & Wire Div., steel and wire works, Donora, has been named manager of operations of the division's Duluth district.

William Rostoker has been promoted to the rank of senior scientist at Armour Research Foundation of Illinois Institute of Technology. Dr. Rostoker joined the Foundation in 1951. Prior to that he taught at the Illinois Institute of Technology and was a lecturer at the University of Birmingham, England.

John E. Osmanski has been appointed supervisor of training for Crucible Steel Co. of America.

Warren G. Rosendahl has been appointed director of manufacturing for the Columbia Machinery & Engineering Corp., Hamilton, Ohio.

W. P. Getty was appointed general manager of steel works, production dept., Jones & Laughlin Steel Corp. **C. C. Henning** has been named general manager of ore mines and quarries and **E. R. Cooper** was named general manager of coal mines.

Jay DeEulis, former engineering editor of *Steel*, has joined Carboloy dept. of General Electric Co., Detroit as technical editor of the news bureau.

— Coming Events —

Feb. 4, AIME, Chicago Section, Chicago Bar Assn., Chicago.

Feb. 13, AIME, Southwestern Section, National Open Hearth Committee, Lennox Hotel, St. Louis, Mo.

Feb. 16-19, AIME, annual meeting, Statler Hotel, Los Angeles.

Feb. 26-28, Indian Institute of Metals, annual general meeting, Bangalore, India.

Mar. 4, AIME, Chicago Section, Chicago Bar Assn., Chicago.

Mar. 7, Symposium on Air Pollution, Wagner College, Staten Island, N. Y.

Mar. 9-11, American Institute of Chemical Engineers, Buena Vista Hotel, Biloxi, Miss.

Mar. 11, AIME, Connecticut Section, Waterbury, Conn.

Mar. 11, AIME, Chicago Open Hearth Local Section, all day meeting, Del Prado Hotel, Chicago.

Mar. 16-20, National Assn. of Corrosion Engineers, annual conference and exhibition, Hotel Sherman, Chicago.

Mar. 18, AIME, National Open Hearth Steel Committee, Roger Young YMCA, Los Angeles.

Mar. 18-20, ASTE, annual meeting, Statler Hotel, Detroit.

Mar. 23-27, ASM, western metal congress and exposition, Pan-Pacific Auditorium, Los Angeles.

April-May, Empire Mining and Metallurgical Congress, Australia and New Zealand.

Apr. 1, AIME, Chicago Section, Chicago Bar Assn., Chicago.

Apr. 12-16, Electrochemical Society, Inc., spring meeting, Statler Hotel, New York.

Apr. 12-May 23, Empire Mining and Metallurgical Congress, Australia-New Zealand.

Apr. 20-22, AIME, National Open Hearth and Blast Furnace, Coke Oven and Raw Materials Conference, Hotel Statler, Buffalo.

Apr. 21, Assn. of Consulting Chemists & Chemical Engineers, Inc., symposium and dinner, Hotel Belmont Plaza, New York.

Apr. 25-May 10, Liege International Fair, Liege, Belgium.

Apr. 26-29, American Institute of Chemical Engineers and **Chemical Institute of Canada,** Royal York Hotel, Toronto.

May 14-16, AIME, Pacific Northwest Metals and Mineral Conference, joint meeting, Metals Branch and Industrial Minerals Div., Ben Franklin Hotel, Seattle.

May 18-22, National Materials Handling Exposition, Convention Hall, Philadelphia.

May 20, AIME, National Open Hearth Steel Committee, field trip.

June 3-7, Chemical Institute of Canada, Windsor, Ont.

June 15-19, Basic Materials for Industry, conference, Hotel Roosevelt; exhibition, Grand Central Palace, New York.

Sept. 21-23, American Mining Congress, Metal and Nonmetallic Mineral Mining Convention, Olympic Hotel, Seattle.

Oct. 27, Assn. of Consulting Chemists & Chemical Engineers, 25th anniversary annual meeting, Hotel Belmont Plaza, New York.

Oct. 28-31, AIME, El Paso Fall meeting, El Paso.

Oct. 29-31, National Council of State Board of Engineering Examiners, Annual Meeting, Plaza Hotel, San Antonio, Texas.

Obituaries

Lucien Eaton, Sr. (Member 1901), Legion of Honor, died on Dec. 9, 1952. Mr. Eaton was a noted mining consultant and former engineer for the Cleveland-Cliffs Iron Co. Born at St. Louis, on July 6, 1879, he was a

LUCIEN EATON, SR.

graduate of Harvard University, holding A.B., M.S., and S.B. degrees. In 1901 Mr. Eaton was an assistant instructor at Harvard and in 1903 joined Cleveland-Cliffs as an assistant engineer. In 1902 he was located at Ishpeming and Ironwood. He was transferred to Iron Belt, Wis. as superintendent of Iron Belt and Shores mines. Mr. Eaton was made superintendent of the Ishpeming district from 1909 to 1929. He was a consulting engineer for the Roan Antelope Copper Co. and Rhodesian Selection Trust, Ltd. from 1929 to 1933. He was also a consultant for various gold mining firms in Australia. In 1938 Mr. Eaton was general manager of the Isle Royale Copper Co. For approximately six years he was located in New York with H. A. Brassert & Co. and was later associated with Pierce Management, Scranton, Pa., for the Turkish Government in Turkey. He was connected with several mining companies and was president-director of the Inca Mining & Development Co., Santo Domingo, Peru. Mr. Eaton was a member of various professional societies. He authored the book *Practical Mine Development and Equipment* and contributed to technical journals.

G. M. Enos (Member 1919), professor and chairman of the Dept. of Metallurgical Engineering, Purdue University died suddenly on Oct. 27, 1952. Dr. Enos was born in Dubuque, Iowa in 1896. He received the degree of Master of Science in metallurgical engineering from Carnegie Institute of Technology after graduating from the South Dakota School of Mines. In 1925 he received a Ph.D. from the University in Cincinnati. Dr. Enos was employed on the staff of the Bureau of Mines from 1921 to 1923 and served on the staff of the dept. of chemical and metallurgical engineering, University of Cincinnati for approximately 16 years. In 1939 Dr. Enos was called to active duty as a Captain in the Specialist Reserve of the Army. He joined the staff at Purdue in 1946 as professor of metallurgical engineering. He was the author of various books and a member of various organizations.

NECROLOGY

Date Elected	Name	Date of Death
1951	T. W. Anderson	Unknown
1935	C. H. Bliem	Unknown
1923	John L. Bray	Dec. 6, 1952
1917	G. Temple Bridgman	Nov. 25, 1952
1945	John Clarkson	June 11, 1952
1907	G. A. Collins	Nov. 12, 1952
1921	F. L. Estep	Dec. 11, 1952
1949	Henry F. Forbes	Sept. 20, 1952
1940	L. E. Hanley	Nov. 15, 1952
1926	H. M. Hartmann	Aug. 17, 1952
1914	William F. Lewis	July 12, 1952
1938	M. B. Lovelace	Apr. 11, 1952
1946	S. S. Marshall, Jr.	Dec. 8, 1952
1921	A. M. McDermott	Unknown
1942	Frederick R. Mitchell	Apr. 28, 1952
1948	O. C. Schmedeman	Dec. 1951
1940	Vivian P. Strange	Apr. 14, 1952
1949	Kolagotla B. Swamy	Unknown
1942	Whitman Symmes	Dec. 3, 1952
1904	R. P. Wheelock	Nov. 17, 1952
1917	Wm. Ryer Wright	Nov. 26, 1952

Proposed for Membership

— Metals Branch AIME —

Total AIME membership on Dec. 31, 1952 was 18,643; in addition 1964 Student Associates were enrolled.

ADMISSIONS COMMITTEE

T. D. Jones, Chairman; Thomas G. Moore, Vice-Chairman; Harold S. Bell, F. W. Hanson, R. H. Chadwick, T. W. Nelson, J. H. Scaff, John T. Sherman, A. C. Brinker, Ivan Given, C. A. R. Lambly, G. P. Lutjen, E. A. Prentis, and C. Leslie Rice, Jr.

The Institute desires to extend its privileges to every person to whom it can be of service, but does not desire as members persons who are unqualified. Institute members are urged to review this list as soon as possible and immediately to inform the Secretary's office if names of people are found who are known to be unqualified for AIME membership.

In the following list C/S means change of status: R, reinstatement; M, Member; J, Junior Member; A, Associate Member; S, Student Associate.

Alabama
Birmingham—Templeton, James B. (J) (C/S—S-J)
Tuscaloosa—Browning, James S. (J)

Arizona
Miami—Napp, Gordon E. (J)

California
Richmond—Butler, Richard C. (J) (C/S—S-J)
San Francisco—Carter, Jackson R., Jr. (J) (C/S—S-J)
San Francisco—Goheen, John L. (M) (R. C/S—S-M)
Selby—Lambe, James N. (M)

Connecticut
Cheshire—Barnes, Elmer S. (M)
Greenwich—Rendahl, Orville B. (M)

Indiana
Gary—Harrington, John J. (J) (C/S—S-J)
Gary—Turman, Robert E. (J) (R. C/S—S-J)

Illinois
Chicago—Edberg, Roy O. (J) (C/S—S-J)
Chicago—Hess, Thomas D. (M)
Chicago—Hoff, William A. (M)
Chicago—Pope, Richard L. (M) (R. C/S—J-M)
Chicago—Zegler, S. Thomas (M) (R. C/S—S-M)

Maryland
Baltimore—Widener, Paul L. (J) (C/S—S-J)
Towson—Lynch, Dunstan W. P. (M) (R. C/S—S-M)

Massachusetts
Malden—Nanis, Leonard (J) (C/S—S-J)
Newton Highlands—Levesque, Pascal (M)

Michigan
Detroit—Chesney, Harvey L. (J) (C/S—S-J)

New Jersey
Maywood—Finder, Carl D. (J) (C/S—S-J)

New Mexico
Silver City—Bosworth, Albert M. (M)

New York
Bayside—Spencer, Chester W. (J) (C/S—S-J)
Brooklyn—Ring, Bernard (A)
Great Neck—Malmlow, Eric G. (A)
New York—Liu, You-Chao (J) (C/S—S-J)
Niagara Falls—Martin, Roy C. (J) (R. C/S—S-J)
Schenectady—Fisher, John C. (M) (C/S—J-M)

Ohio
Cleveland—Hrehov, John G. (J) (C/S—S-J)
Cleveland—Liu, Tien-Shih (J) (C/S—S-J)
Cleveland—Signorelli, Robert A. (J) (C/S—S-J)
Columbus—Bruckart, William L. (M) (C/S—J-M)
Middletown—Ungaro, Salvatore (M)
Shaker Heights—Carpenter, Joel C. (M) (R. C/S—J-M)
Toledo—Baginski, Willi A. R. (M)
Youngstown—Wentz, Ervin L. (M)

Pennsylvania
Abington—Shea, John W. (A)
Birdsboro—Youtz, Earl (J)
McKeesport—Murphy, Robert J. (J) (C/S—S-J)
Phoenixville—Webb, William S. (M)
Pittsburgh—Berger, J. Alfred (M) (R. C/S—S-M)
Pittsburgh—Egan, John J. (M) (R. M)
Pittsburgh—Haus, Walter C. (A)

Texas
El Paso—Plapp, Elmer B. (M)
El Paso—Stocker, James E. (M)

Washington
Richland—Hunkeler, Francis J. (J) (C/S—S-J)
Tacoma—Rosene, Carl J. (M) (C/S—J-M)

Canada
Montreal—Elijah, Leo M. (J) (C/S—S-J)
Montreal—Rehder, John E. (M)
St. Joseph de Sorel—Montpetit, Jean G. (J) (C/S—S-J)
Toronto—Landry, Edward R. (J) (C/S—S-J)

England
Birmingham—Paxton, Harold W. (J) (C/S—S-J)

France
St. Germain-en-Laye—Allard, Marc (M)
St. Germain-en-Laye—Delbart, Georges R. (M)

Germany
Ulm (Donau)—Wieland, Hans (M)

Holland
Eindhoven—Meyering, Jan L. (M)

Mexico
Juarez—Winter, Edward J. (M)
Mexico D.F.—Ehrenberg, Peter R. (J) (C/S—S-J)

Northern Rhodesia
Kitwe—Howd, George T. (J)

Sweden
Surahammar—Ameen, Einar L. (M)

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